DETERMINATION OF FILMING AND ALKALIZING AMINES USING LC-MS AND THE INFLUENCE OF THESE AMINES ON ION EXCHANGE RESIN PROPERTIES

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Major Field: Chemistry

Abstract:

In steam turbine power plants, filming amines are injected into the steam header to coat and protect pipe surfaces against corrosion. Alkalizing amines are added to the boiler feedwater to control pH of the condensate in order to prevent corrosion. Higher concentrations of these amines in the condensate can corrode copper alloys. Moreover, properties and performance of polishing ion exchange resins used to purify the process water can be affected by the use of filming and alkalizing amines. Hence, it is important to monitor and maintain the amine concentration in the condensate. Understanding the effect of the use of these amines on ion exchange resin properties is also very crucial.

In this work, a simple method has been developed for determination of filming and alkalizing amines using liquid chromatography mass spectrometry (LC-MS). Four filming and four alkalizing amines were successfully analyzed. Cyclohexylamine uptake capacity of DOWEX 650C was also determined using the method. To investigate the effect of exposure, one anion and three cation exchange resins were treated with ten different amines including two commercial filming amines. Resin properties were determined for the standard, amine exposed and regenerated forms.

All the resins were fouled due to amine exposure; higher adsorptions were observed by the cation exchange resins compared to the anion exchange resin. A decrease in exchange capacities were found and regeneration did not achieve complete recovery of the ion exchange resin properties. Adsorption of amines and their presence after regeneration were confirmed by LC-MS and fluorometric analysis.

Salt splitting kinetic experiments were also performed. At the end of this research, nanometric aggregates of molybdenum (VI) oxide and tungsten (VI) oxide were prepared using ion exchange resins that can be used for environmental and catalytic applications.

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CHAPTER I

INTRODUCTION

Ion Exchange

The process of exchanging ions between two electrolytes or between an electrolyte and a solid material is known as ion exchange.[1] Since the introduction of this technology in the early 20th century,[2] ion exchange materials have been prepared and used in a wide range of industries including chemical and petrochemical,[3] agricultural, water purification operations, and pharmaceutical.[4] The numerous applications of ion exchange process include: water treatment and softening,[5] reagent purification,[6] catalysis,[7] solvent purification, heavy metal removal [8], and separation of ions. Preparation of high purity water for power generation, electronic and nuclear industries is among the most important uses of ion exchange materials, and is the focus of this dissertation.

Ion exchange is a reversible reaction whereby ions interchange between two media while maintaining charge equivalence. Insoluble solid substances containing exchangeable ions are known as ion exchanges. When introduced to the solution containing ions of same charge, the exchangeable ions can be replaced with ions in the solution.[9] The process can be represented as shown in Figure 1.1.

$$M^+ A^- + N^+ \rightleftharpoons N^+ A^- + M^+$$ Cation Exchange

$$M^+ A^- + B^- \rightleftharpoons M^+ B^- + A^-$$ Anion Exchange

Figure 1.1: Ion exchange process

The charge neutrality is preserved by the exchange of equivalent amounts of charge. The exchange capacity of an ion exchanger is generally reported as the total content of exchangeable ions present per kilograms or liter of the material.[10] The basic requirements for a good ion exchange material are: a hydrophilic inert structure that allows hydrated ions to diffuse within the matrix, high exchange capacity, and stability of the material.

Ion Exchange Resin:

Ion exchange resins are the most commonly used ion exchange materials. These are high molecular weight, three dimensional, cross-linked polymer matrix of hydrocarbon, functionalized with ionic groups such as sulfonic acid.[9] Ions present in the resin beads can be exchanged with the ions in the solution they are in contact with. The ion exchange process in a resin bead is shown in Figure 1.2.

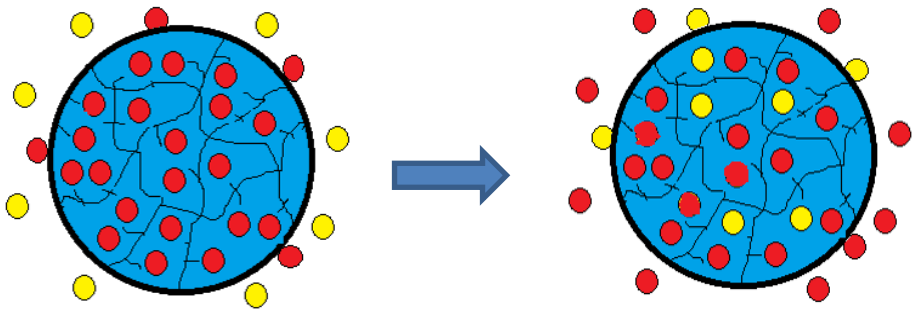


Figure 1.2: Ion exchange in resin bead

Types of Ion Exchange Resin:

Ion exchange resins are classified according to the functional group present in the resin.

1) Cation exchange resin
    A) Strong acid (sulfonic acid)
    B) Weak acid (carboxylic acid, phosphoric acid)
2) Anion exchange resin
    A) Strong base (quaternary amino)
    B) Weak base (primary, secondary, tertiary amino)
3) Chelating resins

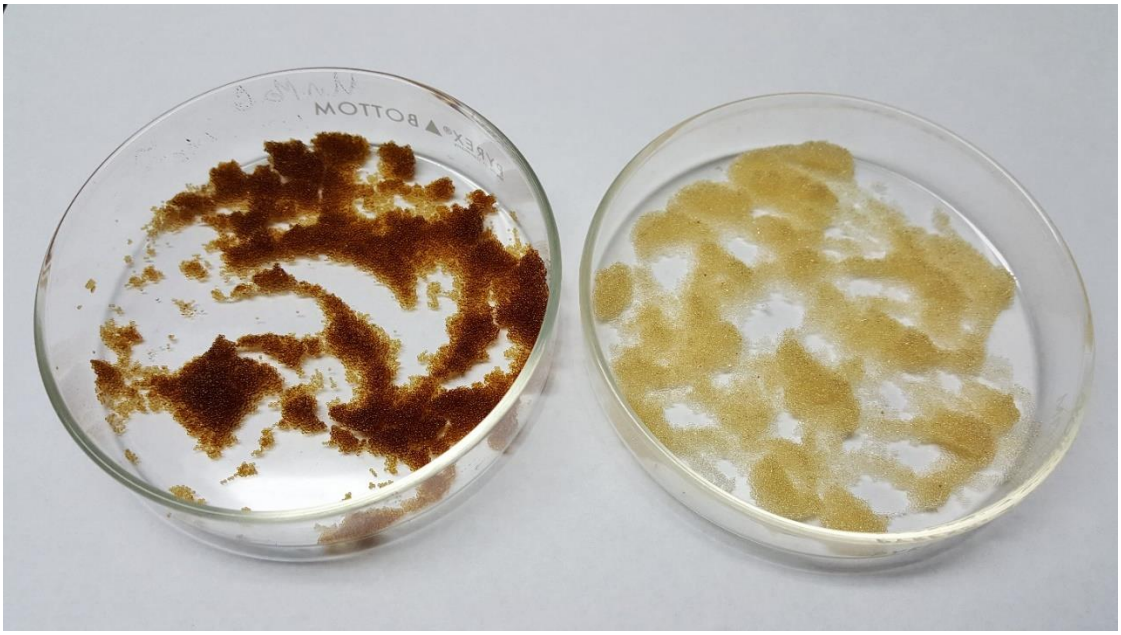


Figure 1.3: DOWEX 650C strong acid cation exchange resin (left), DOWEX 550A strong base anion exchange resin (right)

Synthesis of Ion Exchange Resin:

The first cation exchange resin, which was an extremely weak cation exchanger, was prepared by the condensation polymerization of phenol and formaldehyde.[11] Later, cationic and anionic groups with high acid and base strengths were synthesized with much higher capacities and pH working range. Commonly used strong acid cation exchange resins contain sulfonic acid ($-SO_3H$) groups and weak acid cation exchange resins are made with carboxylic acid (-COOH) groups.[12]

The resin backbone consists of an addition copolymer prepared from polystyrene, and divinyl benzene is used as the cross-linking agent. These polymers have higher chemical and thermal stability, and degree of cross linking and particle sizes are also adjustable. The sulfonic acid groups are introduced by treating with sulfuric acid or chlorosulfonic acid.[13] The reaction is shown in Figure 1.4.

Condensation polymerization of aromatic amines and formaldehyde was used to prepare the first anion exchange resins. Weak base anion exchange resins contained weak base amino groups such as $-NH_3^+$ and $R_2NH_2^+$. Strong base quaternary ammonium groups (N^+R_3 groups) are present in strong base anion exchange resins.[14] While quaternary amines are non-basic, these resins typically have hydroxide (OH^-) as the counter ion, hence they are strongly basic. Anion exchange resins are prepared by chloromethylation of polystyrene beads followed by treatment with ammonia or primary, secondary or tertiary alkyl amines. Reaction with tertiary amine produces strong base anion exchange resins containing quaternary ammonium groups. The synthetic process is shown in Figure 1.5.

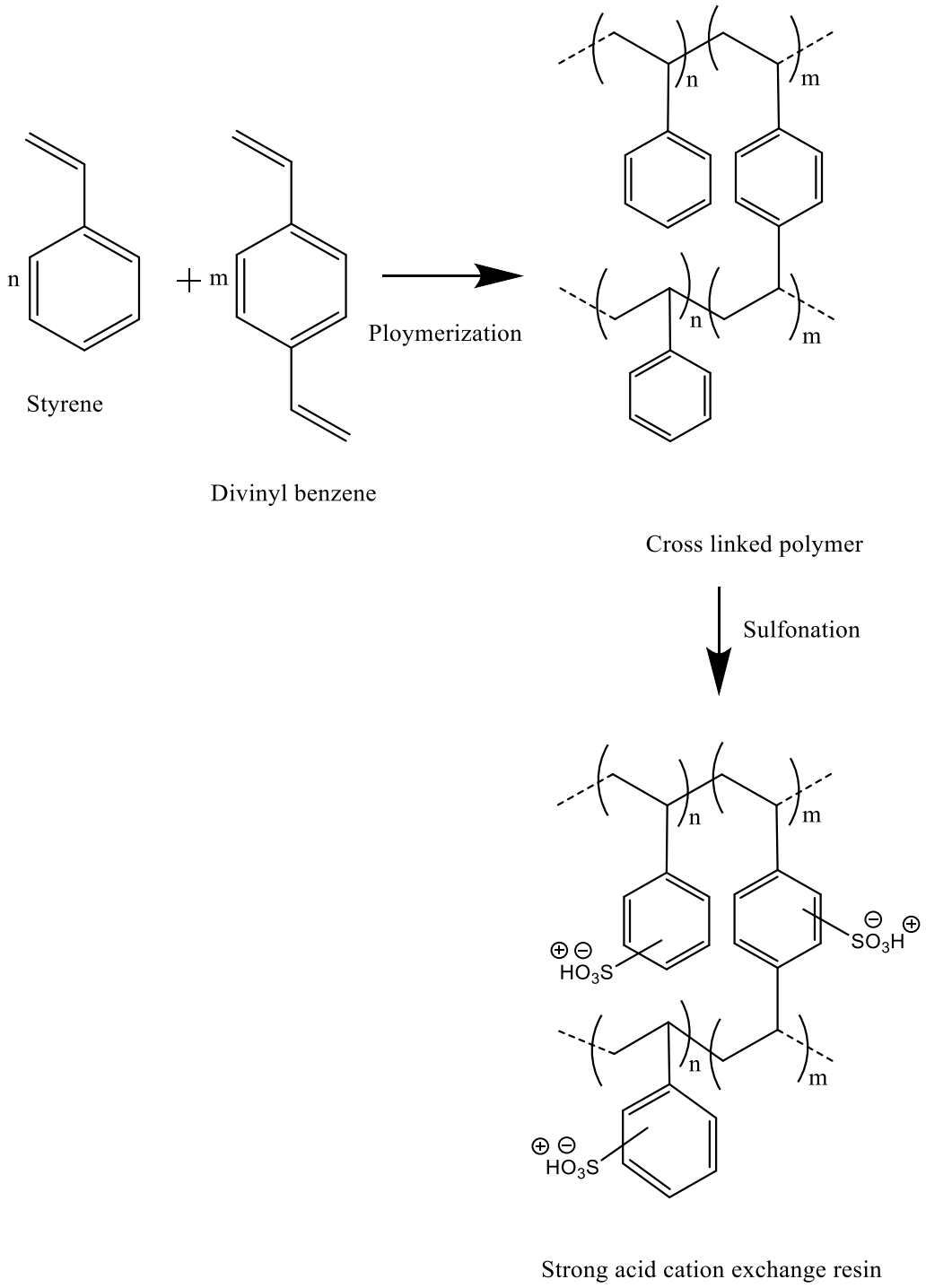
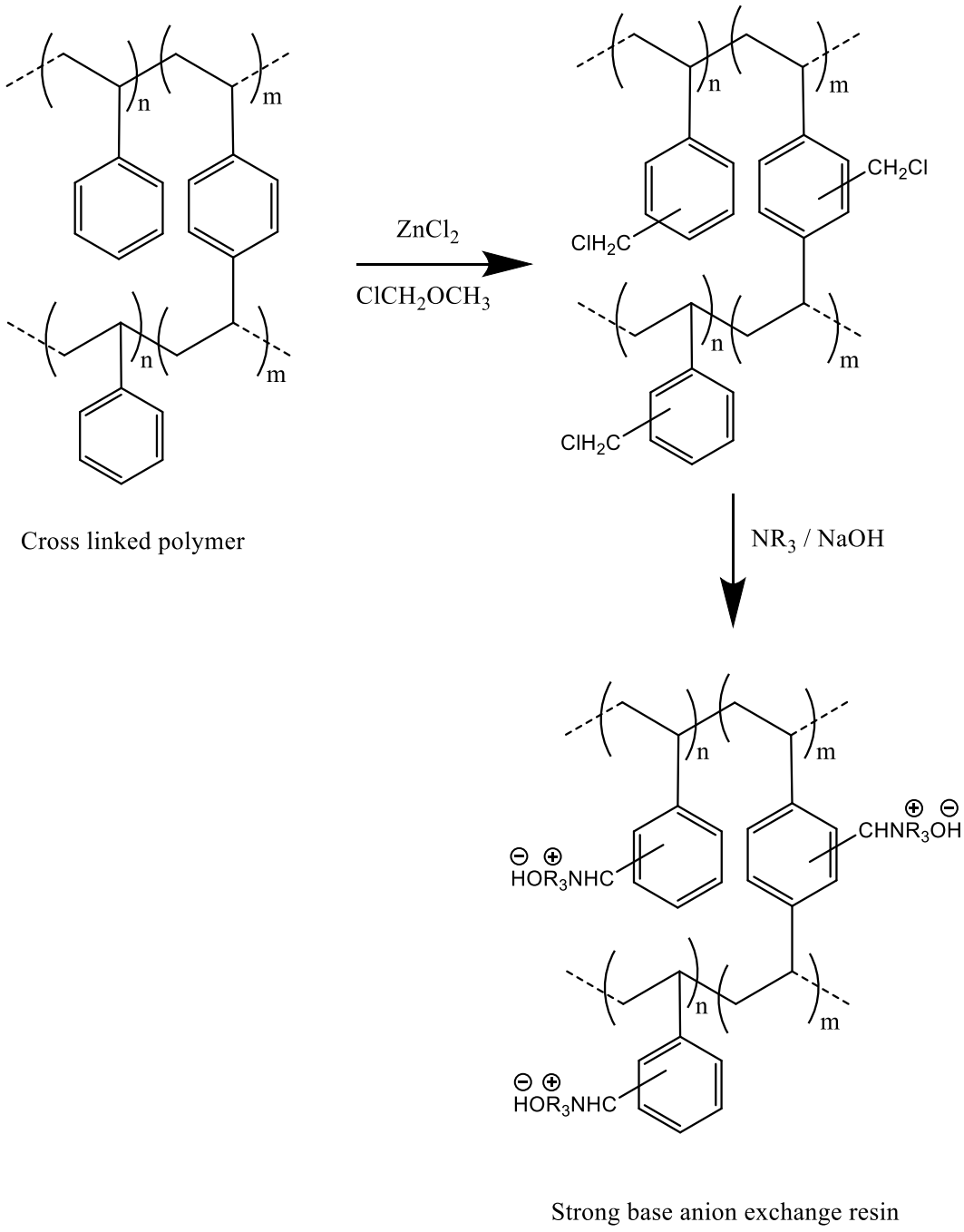


Figure 1.4: Synthesis of strong cation exchange resin



Cross linked polymer

Strong base anion exchange resin

Figure 1.5: Synthesis of strong base anion exchange resin

In general, resins contain 8-12% divinyl benzene. A controlled, appropriate degree of crosslinking is necessary to maintain the resin stability and proper swelling of the resin beads to a certain extent so that the solution containing ionic species that can interact within the matrix.[15] Lower crosslinking allows the resins to swell more but they are also soft, on the other hand, highly cross linked resins show higher mechanical stability with lower swelling, and much slower ion exchange kinetics.

Ion Exchange Resin Properties:

Important physical and chemical properties of ion exchange resins are:

- Appearance and color: Resins can have different colors depending on type and ions present.
- Bead size and shape: Usually spherical beads with size of 1 μm to 2000 μm.
- Exchange capacity: Equivalent moles of exchangeable ions per liter or kilograms of resin.
- Apparent density: Density of swelled resin.
- Moisture content: Water content based on the anhydrous weight of the resin.

Condensate System and Condensate Recovery:

Steam turbine power plants are good example of condensate systems. Steam is produced by heating water at high temperature and pressure in a boiler. Steam leaves the boiler through piping and transfers latent heat to heat exchanger or steam jacket.[16] After heat transfer, steam condenses in the pipe as pure hot water which is known as condensate. The water returns to the boiler, and reused for steam generation. Figure 1.6 shows a flow diagram of condensate system and condensate recovery.

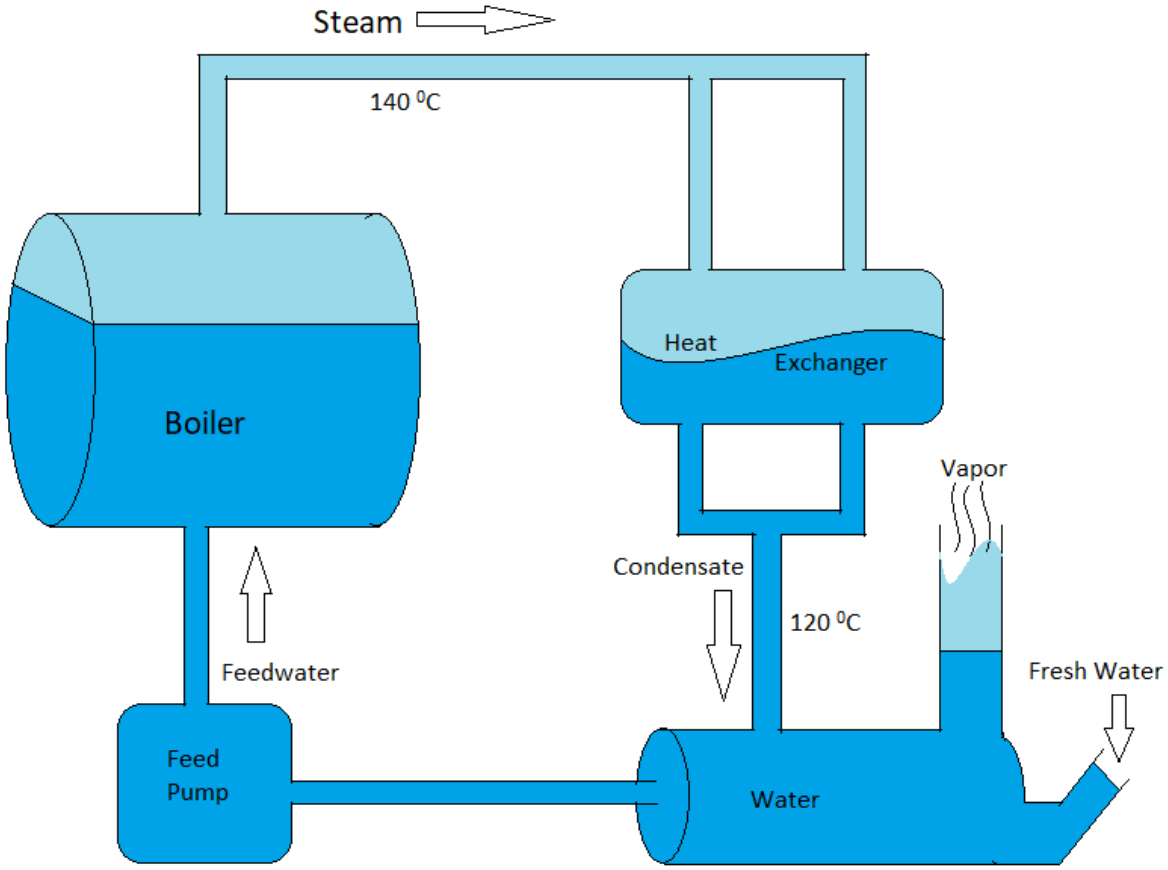


Figure 1.6: Condensate system

Condensate recovery is very important in the industries due to several reasons.

- Condensate contains a significant amount of sensible heat, returning to boiler can reduce fuel consumption up to 20%
- Reuse of condensate reduces total water use in the system
- Cost of water treatment is reduced since condensate is pure water

Ion Exchange Resin and Ultrapure Water:

One major application of ion exchange resin is, their use in condensate systems as condensate polishers to generate ultrapure water.[17] Water is passed through a series of ion exchange resin columns containing cation, anion, or mixed bed resins to achieve high purity to levels of parts per trillion. Ultrapure water is used to generate saturated steam in a steam turbine power plant. A high purity of boiler feedwater is essential to prevent corrosion and deposition of contaminants on boiler and piping surfaces.[3] Figure 1.7 shows a general scheme of a steam turbine power plant.[18]

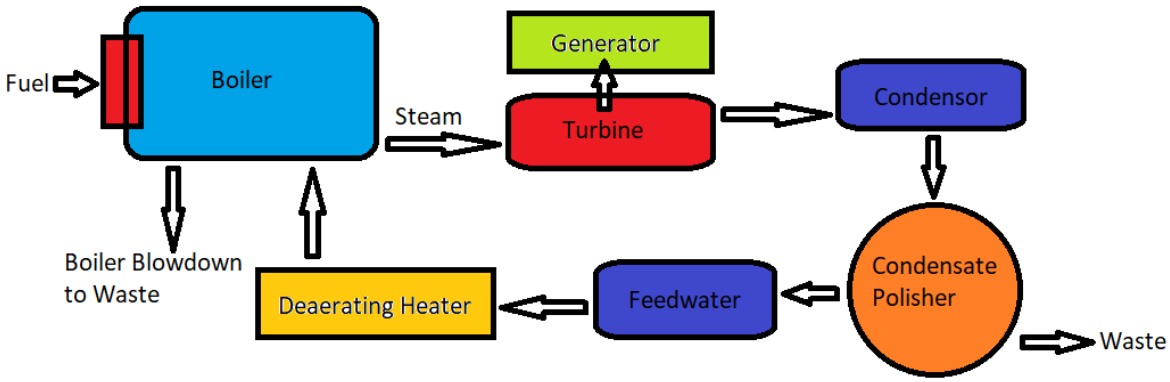


Figure 1.7: Steam turbine power plant [18]

Corrosion and deposition of scale from impure water can cause power plant shutdown, repair or replacement of parts can be very costly. A power plant failure can also lead to accidents, such as the partial core meltdown at the Three Mile Island reactor in Middletown, PA in 1979.[19] Radioactive gases and water were spread across the area, thousands of people had to move to safer places, and the overall loss was close to $2 billion.[20] Evidence from the investigation showed that the trouble started in the condensate polisher system.

Corrosion Due to Dissolved Gases, and Corrosion Inhibitors:

As condensate cools down, it dissolves CO_2, that leads to the formation of carbonic acid. Dissociated carbonic acid makes the water slightly acidic, this is a major reason for corrosion.[21] At elevated temperature and pressure, and in presence of oxygen, the corrosion process accelerates.[22-23] Weakly basic organic compounds, volatile short chain amines, known as alkalizing or neutralizing amines are used as pH control agents.[24] Long chain water insoluble amines are also used as corrosion inhibitors to coat and form a protective layer on the metal surfaces. These amines are known as filming amines.[25] A higher concentration of these corrosion inhibitor amines can have adverse effects. Development of a simple method for analyzing amines to monitor amine concentration in a condensate system is an important goal of this study.

Resin – Amine Interaction:

A secondary problem arises when corrosion inhibitor amines come in contact with polishing ion exchange resins. Filming and alkalizing amines can foul ion exchange resins and decrease resin performance and affect other resin properties.[26] Active sites in the cation exchange resins can be occupied by these amines and reduce exchange capacity. Filming amines can be adsorbed to the

surfaces and polymer backbones of resins blocking access to incoming ions.[27] Replacement of functionality in the anion exchange resins can reduce their effectivity. This investigation sought to determine how exchange capacity and other resin properties are affected by interaction with different corrosion inhibitor amines. The ion exchange kinetics of ion exchange resins can also be affected due to fouling by the amines. Effect on ion exchange kinetics was also looked at in this study.

Preparation of Spherical Aggregates of Nanometric Metal Oxides Using Ion Exchange Resins:

Metal loaded ion exchange resins can be used to prepare spherical aggregates of nanometric metal oxides. Using the morphology of the ion exchange resin beads, ceramic replicas with perfect size and shape could be prepared. Such materials can be useful for water treatment and catalytic operations.[28] Group (VI) transition metals show very rich chemistry due to their partially filled d-orbitals. Molybdenum and tungsten oxides have received much attention for their useful properties.[29] In this research, nanometric molybdenum (VI) oxide and tungsten (VI) oxide were synthesized and characterized.

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CHAPTER II

A SIMPLE METHOD FOR THE DETERMINATION OF ALKALIZING AND FILMING AMINES USING LIQUID CHROMATOGRAPHY MASS SPECTROMERTY (LC-MS)

Corrosion in Condensate Systems:

In a steam generator, water is heated to steam and heat is transferred to heat exchanger. Condensed steam or condensate is the pure hot water after heat exchange.[1] As condensate cools down, CO_2 dissolves into water to produce carbonic acid. Dissociated carbonic acid produces hydronium ions that oxidize steel. The formation of carbonic acid is shown in figure 2.1.

Figure 2.1: formation of carbonic acid

At high temperature and pressure, and in presence of oxygen, the corrosion accelerates.[2] Organic amines are widely used as corrosion inhibitors in condensate systems. They can work in two ways: maintaining the pH close to 7, and forming a coating on metal surface that prevents corrosive species to come in contact with the metal.

Alkalizing / Neutralizing Amines:

Alkalizing or neutralizing amines are shorter chain, water soluble, and volatile amines acting as pH control agent due to their mild basic nature.[3] Since they are volatile, they can be directly added to the boiler feedwater. Alkalizing amines volatilize, react with carbonic acid and control condensate return line corrosion by maintaining the pH of the water. A few common alkalizing amines are listed in figure 2.2.

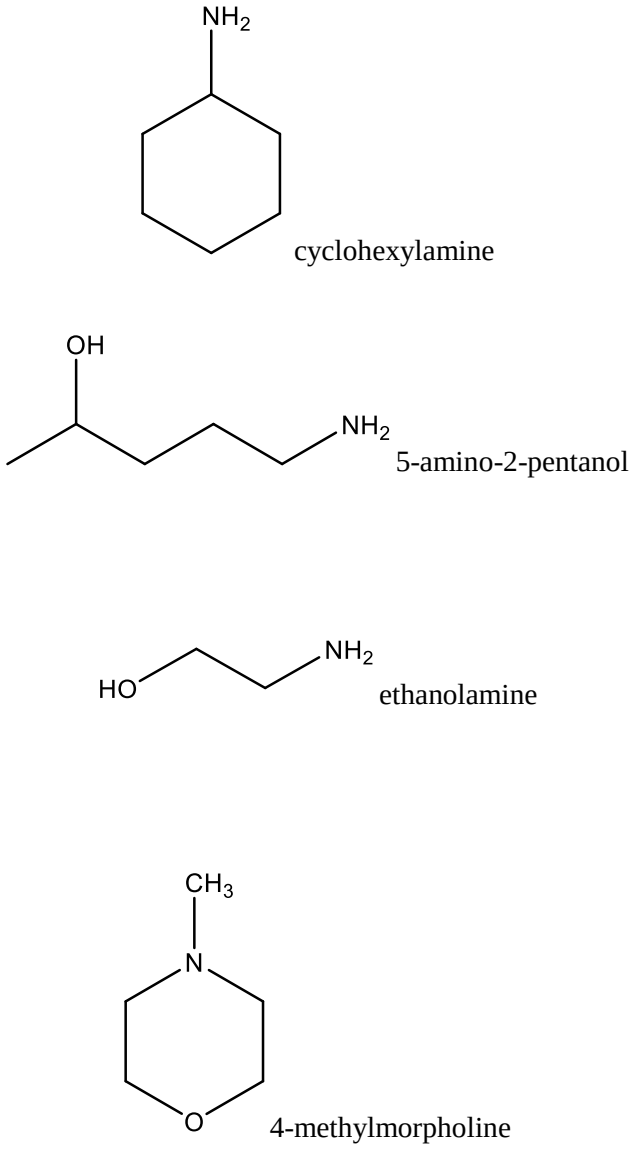


Figure 2.2: Few common alkalizing amines

Filming Amines:

Filming amines are long chain, water insoluble amines those cannot be added to the boiler feedwater directly since they are nonvolatile.[4] These amines are added to the steam header and they coat the inner surface of the metallic piping forming an oily thin film. It prevents the metal surfaces from coming in contact with corrosive species and thus protect the surface from acid and oxygen pitting.[5]

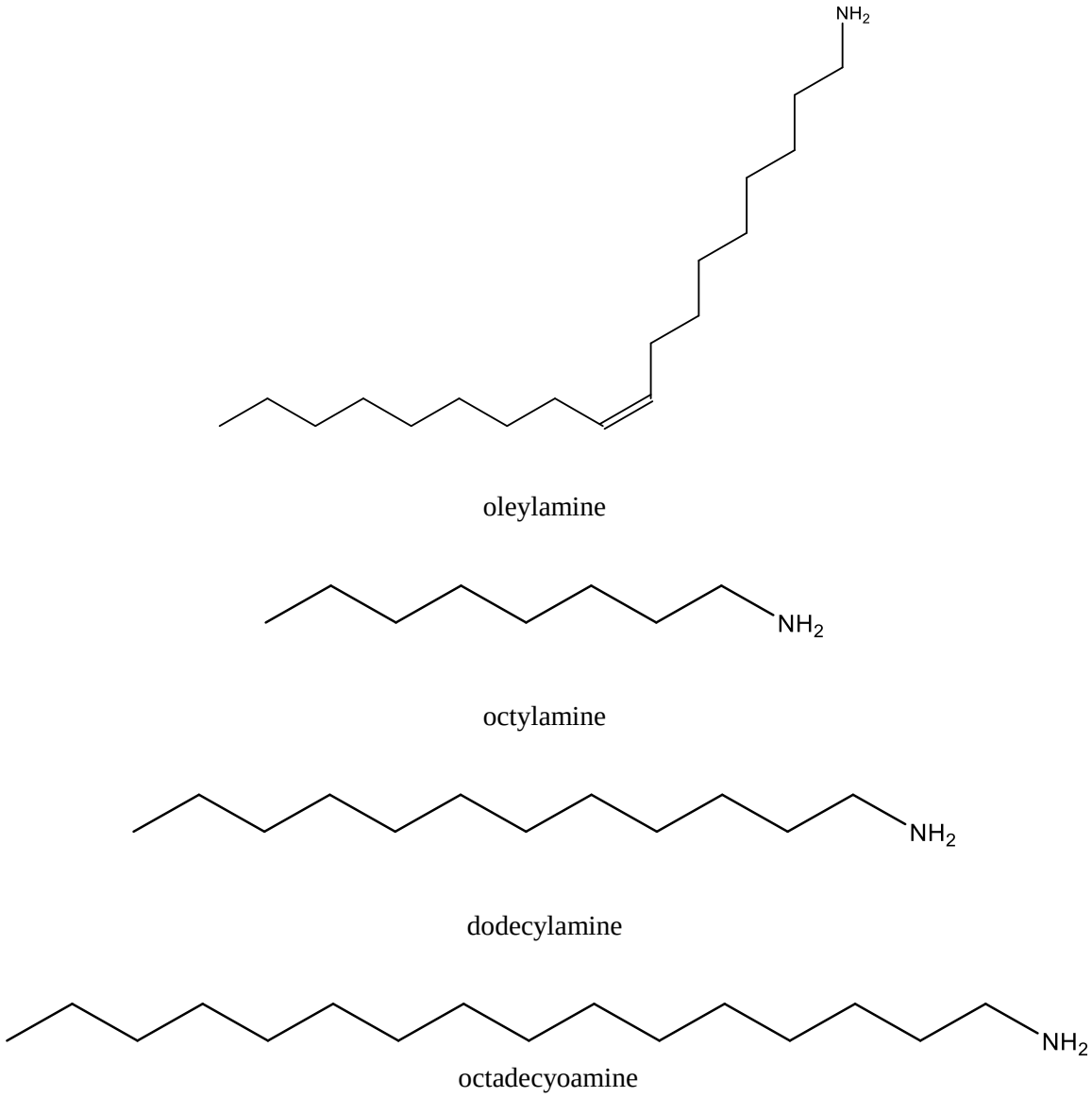


Figure 2.3: Common filming amines

The hydrophobic oily coating also keeps the metal surfaces clean and increase heat transfer. Few common filming amines are shown in figure 2.3. Commercially used corrosion inhibitors are usually a mixture of two or more amines containing both alkalizing and filming amines.

Importance of Analyzing Amines:

Higher concentration of amines can be corrosive to copper alloys. At high pH (above 9) corrosion of copper alloys starts to accelerate. Figure 2.4 shows a generalized relationship between carbon steel and copper alloy corrosion rate with change of pH of condensate.[6]

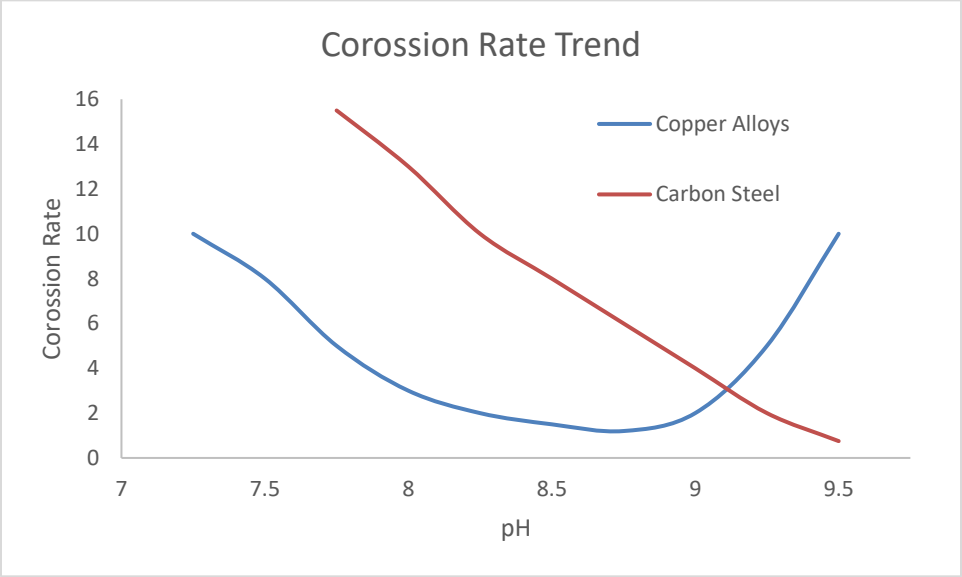


Figure 2.4: Corrosion rate of carbon steel and copper vs pH [6]

Residual amines reaching condensate polisher resins can foul them and reduce resin activities[7] Therefore, this is very important to analyze the concentration of amines at regular intervals and maintain proper pH to ensure the safety of the system.

Current Methods:

Analysis of amines is difficult due to their basic character. Most commonly used methods are:

- Spectrophotometric
- Gas Chromatography
- Fluorometric
- Rose Bengal (colorimetric)

A spectrophotometric method involves pretreatment of the amine sample to produce a colored complex that can be analyzed using UV-visible spectrophotometer.[8] The process also requires maintaining of pH using buffer solution.[9] Gas chromatography is a direct injection method but this is not suitable for long chain filming amines. Fluorometric method also requires pretreatment of the amine solution and maintaining of pH using buffer solution.[10] Moreover, the reagents are expensive. Rose Bengal method is a proprietary colorimetric method, reagents can be purchased only from BKG water solutions, and it also requires specific instrumental set up.

Limitations and Scope of Developing New Method:

The major limitations of the current analytical methods for amine analysis are:

- Time consuming pretreatment required.
- Buffer solutions required for some of the methods, spectrophotometric method requires a 1.8 pH buffer.
- Some of the methods require use of expensive reagents, flourascamine is required for fluorometric method.

- Current methods are mainly designed to analyze individual amine only or total amine content in a mixture, different amines in a mixture cannot be analyzed.

The goal of this study was to develop a method for amine analysis that can overcome such limitations. The main objectives of this study were to:

1. Develop a method that is simple and easy
2. Can be done using inexpensive reagents and available instruments
3. Method that allows direct analysis of the amine samples without pretreatment
4. Can analyze the amines at the industrial concentration range
5. Different amines in a mixture can be analyzed

Experimental:

Materials:

Alkalizing amines used for the analysis were: Cyclohexylamine (Sigma – Aldrich), 5-amino-2-pentanol (Sigma – Aldrich), Ethanolamine (Alfa Aesar), and 4-methylmorpholine (Sigma – Aldrich). Since alkalizing amines are water soluble, solutions at a range of $1x10^{-4}$ to $5x10^{-4}$ M were prepared in deionized water for analysis.

Filming amines those were used were: Octadecylamine (Alfa Aesar), Dodecylamine (Aldrich), Oleylamine (Tokyo Chemical Industries Co. Ltd.), and Octylamine (Acros Organics). Filming amines are water insoluble. $1x10^{-4}$ to $5x10^{-4}$ M solutions in isopropanol (Pharmco Aaper) were prepared. All the amines were used without any further purification. HPLC grade acetonitrile (BDH VWR analytical) and deionized water prepared at 18 mega-ohms were used as mobile phase of liquid chromatography mass spectrometry (LCMS). Trifluoroacetic acid obtained from Kodak was used to acidify the mobile phase.

Method:

The instrumentation and conditions for amine analysis were:

- Instrument: Shimadzu LCMS-2010
- LC column: C-18
- Injection volume: 3 µL
- Mobile phase: 75% Acetonitrile (0.01% trifluoroacetic acid), 25% Water (0.01% trifluoroacetic acid)
- Flow rate 0.25 mL/min
- Analysis time: 20 – 40 min
- Mass spectrometer mode: Scan
- Mass scan: 50 – 500 m/z

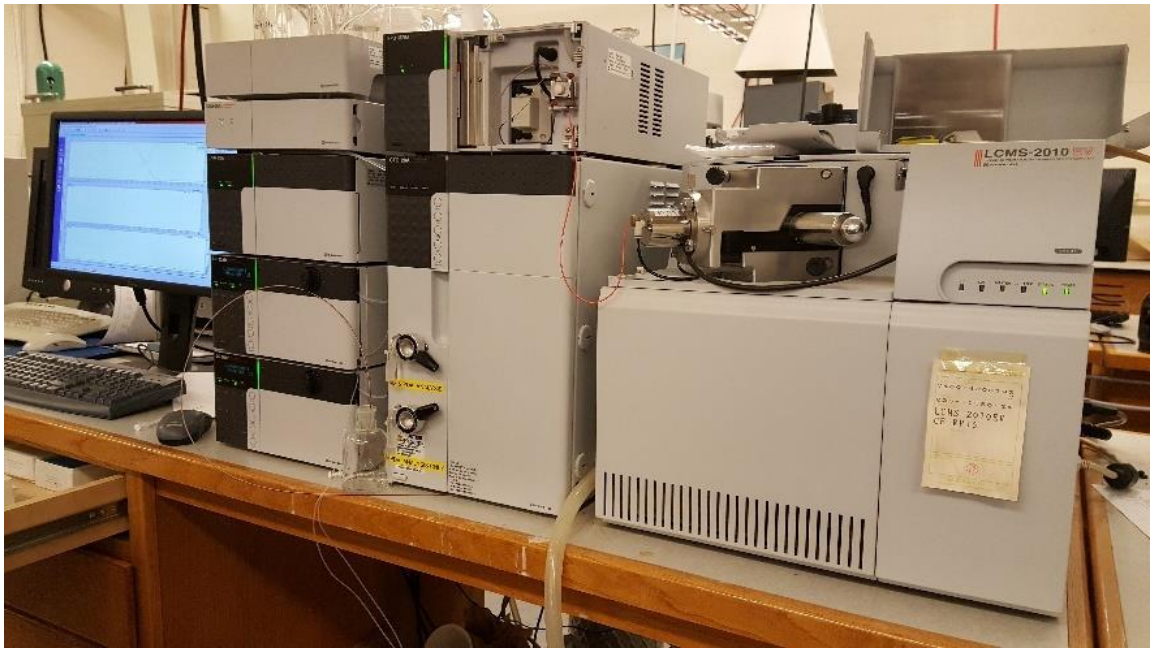


Figure 2.5: The experimental setup using LCMS 2010

Results:

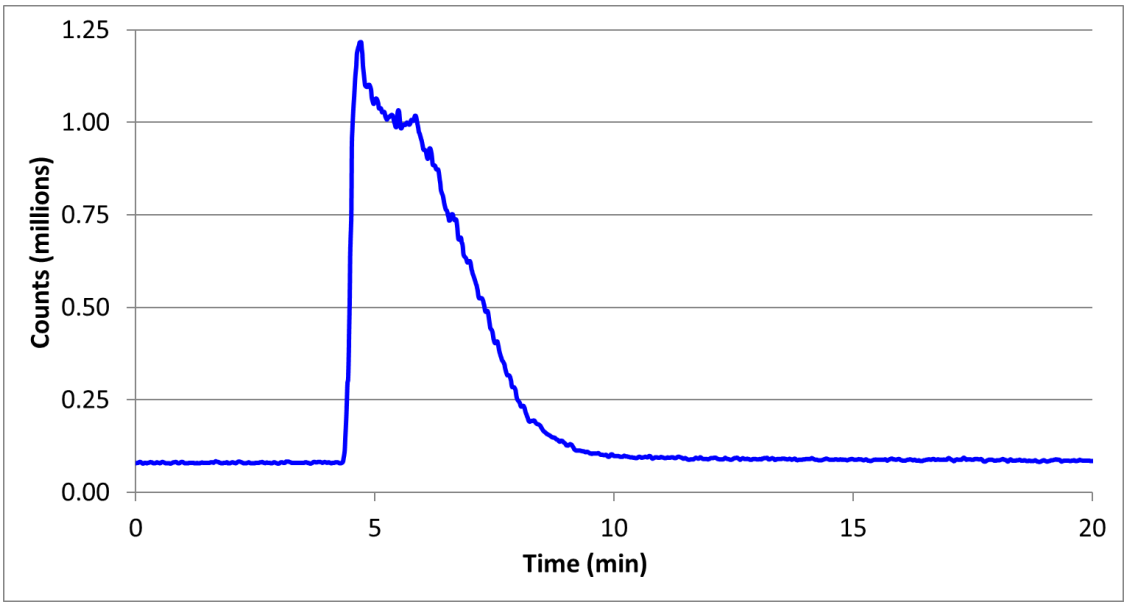
The characteristic peaks were found to be at m/z values that corresponded to M (mass of amine) + 1 (proton) + 1 or 2 A (mass of acetonitrile). The following table shows the retention time for different amines and characteristic peaks in mass spectra:

Amine	Retention time, min	Characteristic peak m/z
Cyclohexylamine	4.7	182
5-amino-2-pentanol	4.4	186
Ethanolamine	4.3	144
4-methylmorpholine	4.4	143
Oleylamine	20.7	309
Octylamine	5.4	170
Dodecylamine	7.3	227
octadecylamine	29.2	311

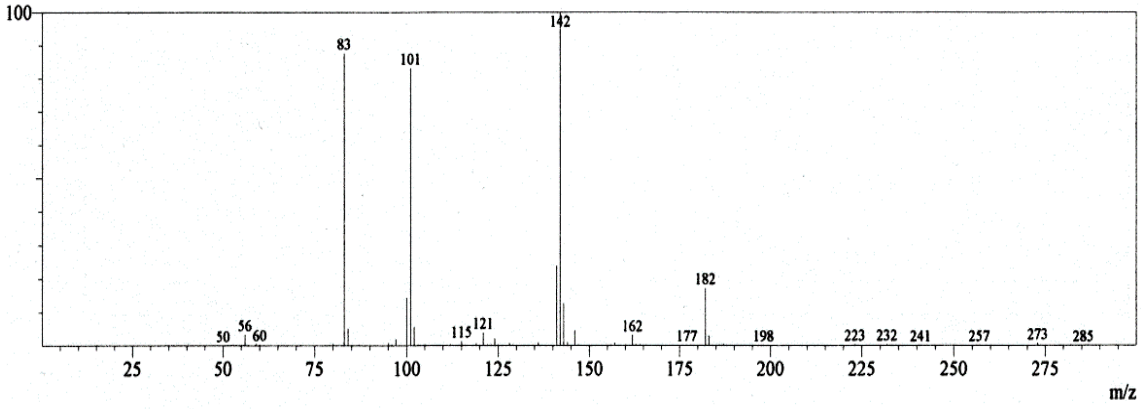
Table 2.1: Amine analysis, retention times and characteristic peaks

The peak areas of the characteristic peaks were calculated and plotted against concentration to generate the calibration curves. Since the area of specific m/z can be calculated separately using the software, different amines from a mixture can be separated by their characteristic peaks even if the retention times overlap. Commercial filming amines that contain a mixture of two or more amines can be easily analyzed using this method. Amines are eluted with an trifluoroacetic acid solution so there is a complex equilibrium between both protonated and unprotonated amines bound and unbound to the chromatographic column. This leads to rather broad peaks that could be sharpened with very high acid concentrations but these would be deleterious to the column. Despite the broad peaks, good reproducibility and accuracy were obtained.

Sample Spectra: Cyclohexylamine



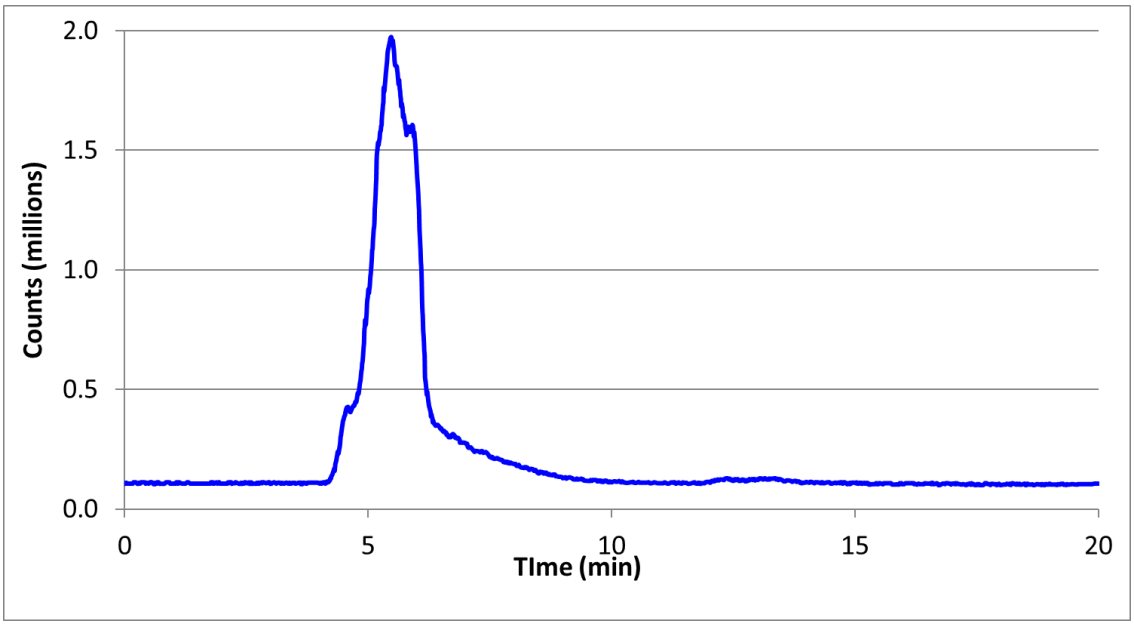
Cyclohexylamine peak at m/z = 182



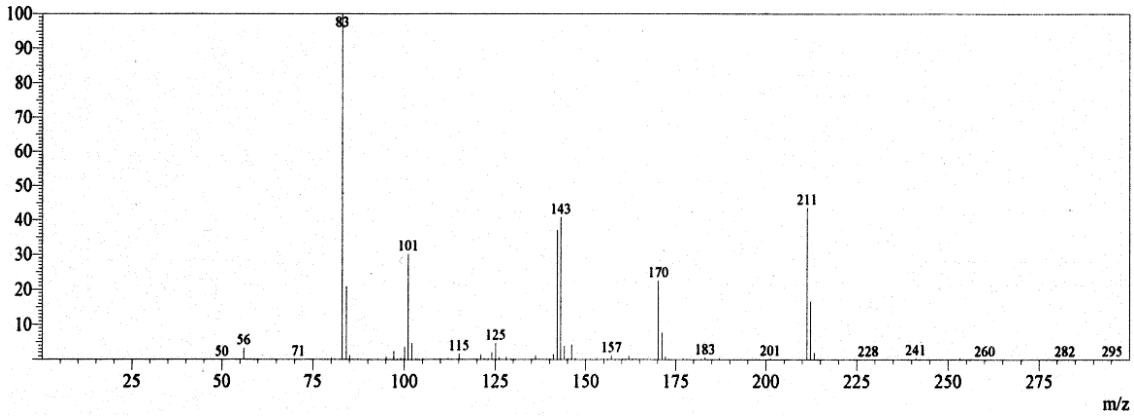
Mass spectra at 5 min

Figure 2.6: Sample spectra for cyclohexylamine

Sample Spectra: Octylamine



Octylamine peak at m/z = 170



Mass spectra at 5.5 min

Figure 2.7: Sample spectra for octylamine

Calibration Curves:

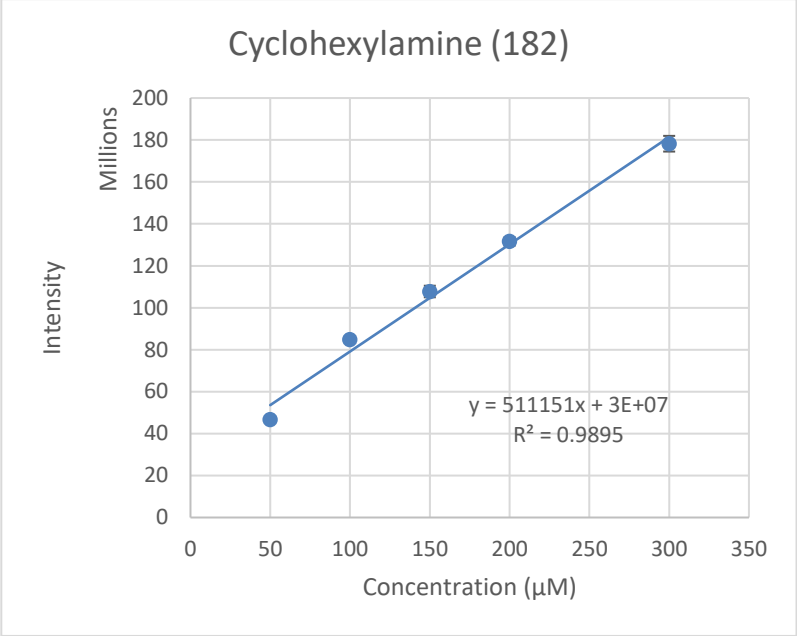


Figure 2.8: Cyclohexylamine calibration curve

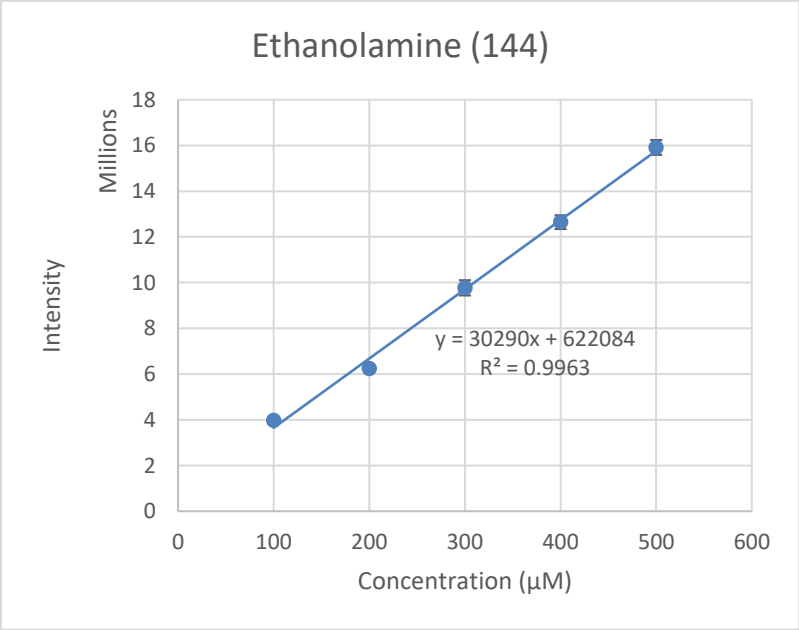


Figure 2.9: Ethanolamine calibration curve

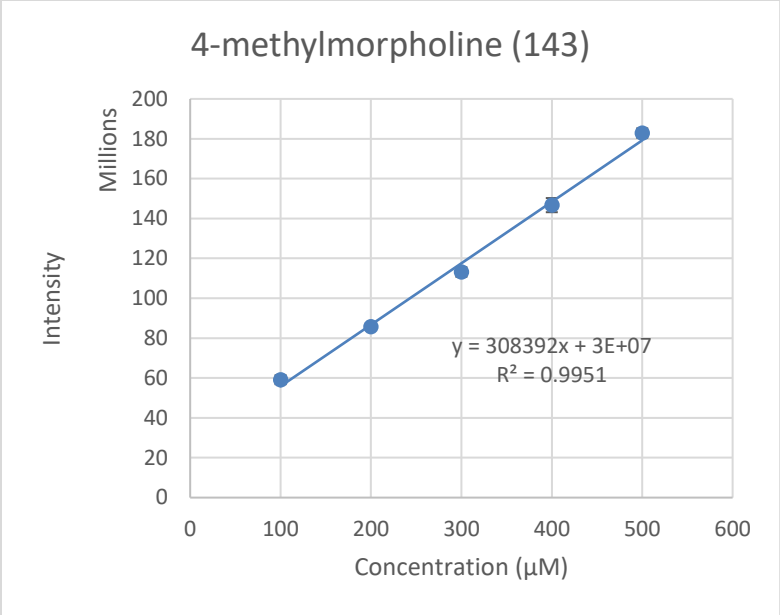


Figure 2.10: 4-methylmorpholine calibration curve

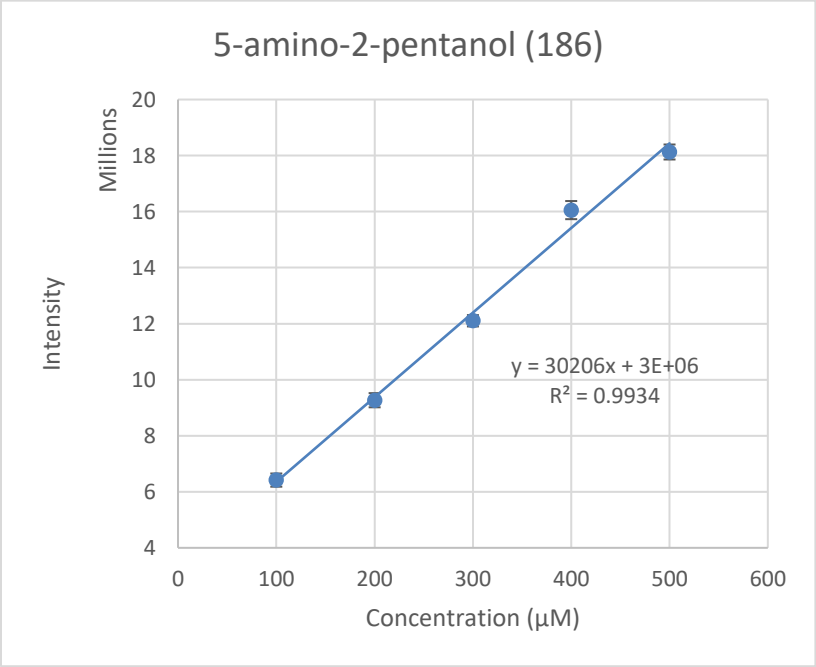


Figure 2.11: 5-amino-2-pentanol calibration curve

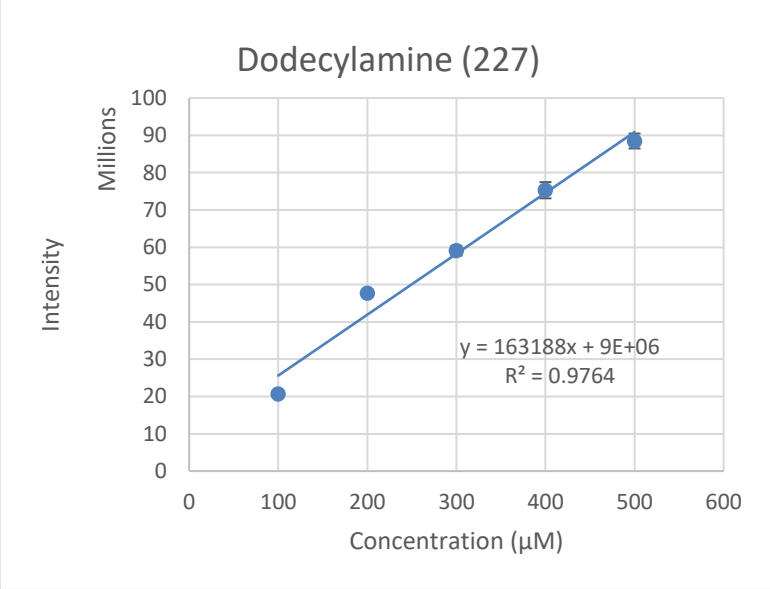


Figure 2.12: Dodecylamine calibration curve

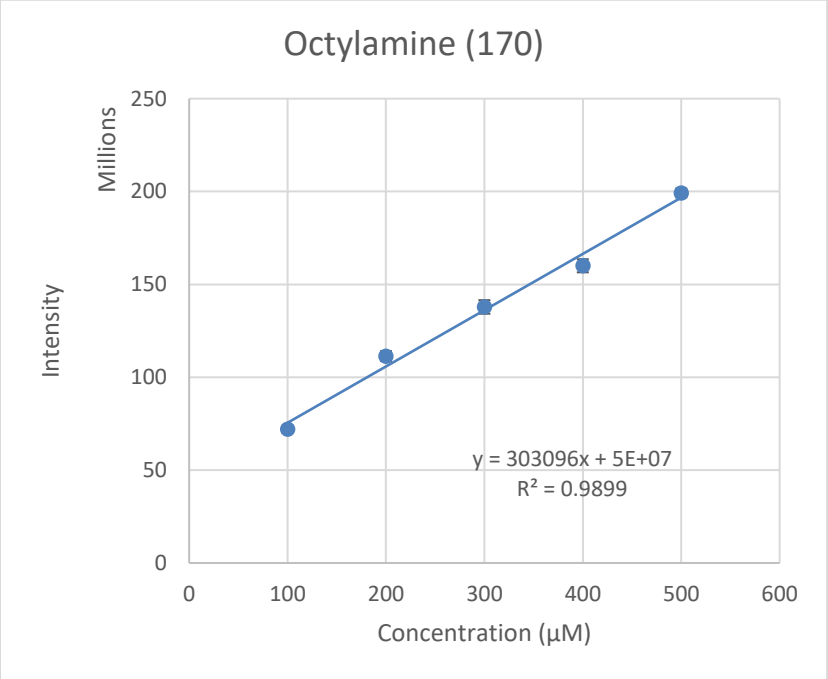


Figure 2.13: Octylamine calibration curve

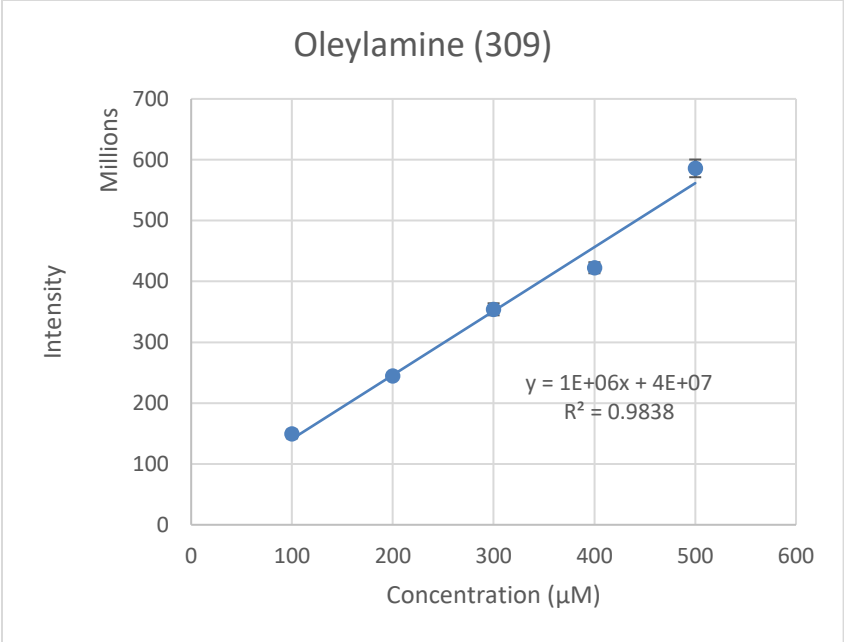


Figure 2.14: Oleylamine calibration curve

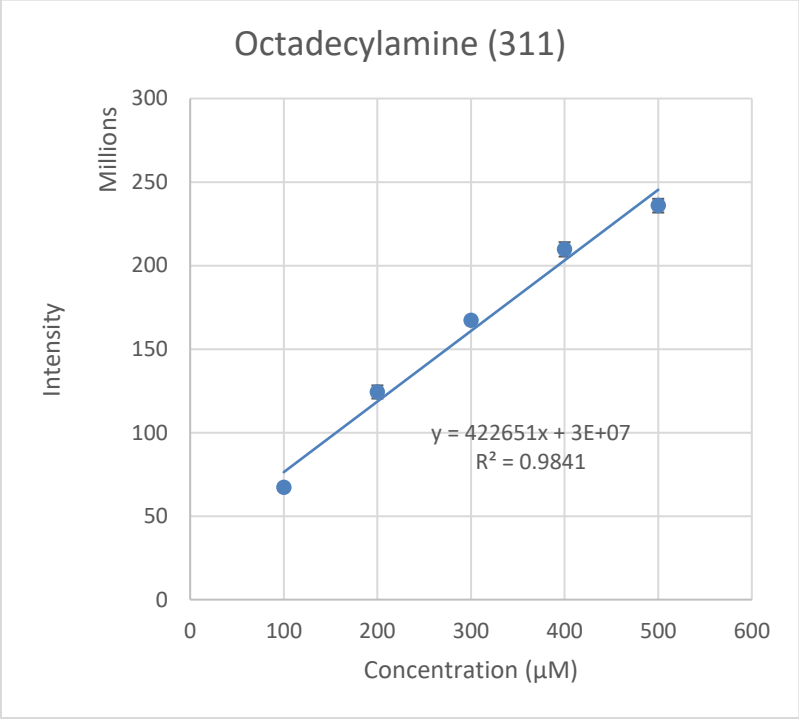


Figure 2.15: Octadecylamine calibration curve

Limit of Detection (LOD):

The detection limit of the method was estimated as the three times of the standard deviation calculated from a number of blank samples.[11] The detection limit out of 25 measurements was calculated as $1x10^{-5}$ M. To calculate the limit of detection, the blank sample signal was integrated at the retention time where characteristic peak of the corresponding amine was found. The concentrations were calculated from the calibration curve. Using the concentration and average concentration data, the standard deviation was calculated. Three times of the standard deviation was used as limit of detection.

Conclusion:

A simple method was developed using LCMS. Amine samples can be injected directly for analysis without pretreatment and use of buffer or expensive reagents. Filming and alkalizing amines, both can be analyzed quantitatively, mixture of amines can also be analyzed using this method without interference. All alkalizing amines show a retention times close to 4 minutes but due to difference in m/z, they can be analyzed in a mixture. Filming amines show longer retention times with increasing molar mass. The method was suitable for the industrial concentration range of filming and alkalizing amines used in the condensate systems. The three factors that contribute to liquid chromatography peak broadening are: column, mobile phase, and sample injection. Interaction with the stationary phase, column void, column length, and silica purity are important. The mobile phase composition, pH of the mobile phase, and the flow rate also contribute. Stronger solvent compared to mobile phase, and larger injection volume can also cause broadening. In future work, experiments will be performed changing column parameters to improve the results. Experiments using gradient mobile phase, change of solvent, and increasing flow rate will also be useful.

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CHAPTER III

IMPACT OF ALKALIZING AND FILMING AMINES ON EXCHANGE CAPACITIES OF ION EXCHANGE RESINS

Exchange Capacity of Ion Exchange Resins:

Ion exchange resins are functionalized cross-linked polymers. They contain specific amount of ion exchange groups or active sites. The measure of exchangeable ions present in the resin is called the exchange capacity.[1] It is expressed in terms of equivalent moles of monovalent ions per liter of resin (mol-eq/L) for wet resins, or equivalent moles of monovalent ions per kilograms of resins (mol-eq/kg) for dry resins.

Significance of Exchange Capacity:

Exchange capacity is the measure of exchangeable sites available. As impure water is passed through the resin bed at a certain rate, the contaminant ions are exchanged at the ion exchange sites. With time, ion exchange sites are taken, and at a certain time when most of the sites are occupied, the rate of exchange becomes slow and some of the contaminant ions leave the resin bed without having the time to exchange, known as kinetic leakage.

This lead to breakthrough point when resin column fail, contaminant ion concentration starts to increase rapidly.[2] Soon all the exchangeable sites are occupied, the column becomes saturated, and total exchange capacity is lost.

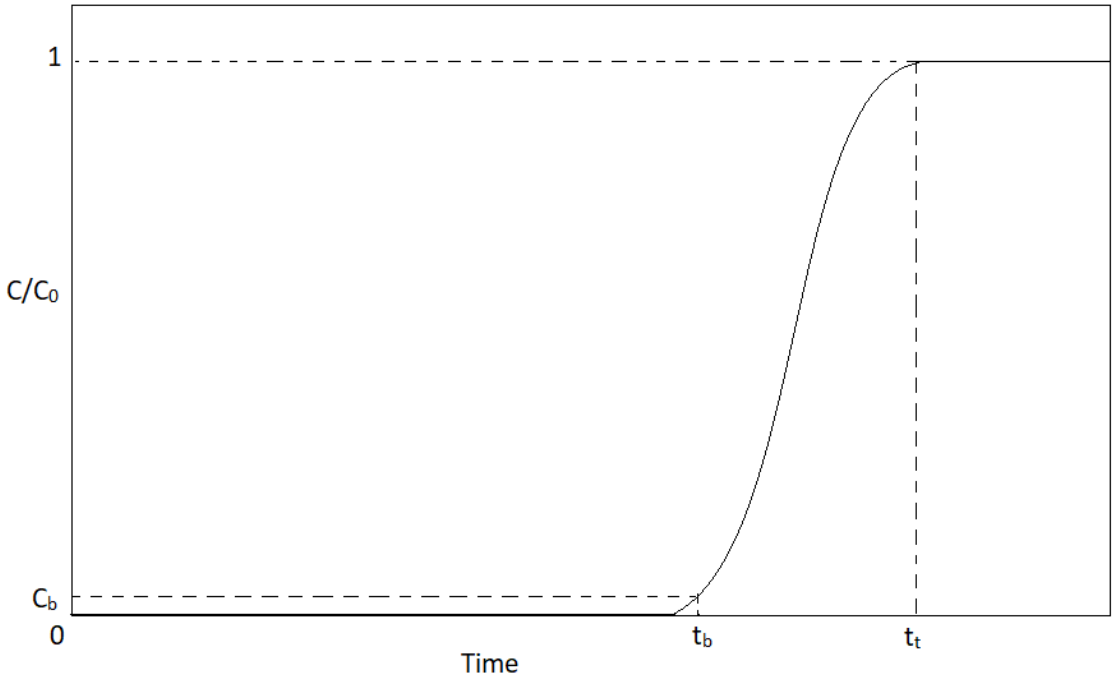

Figure 3.1: Breakthrough curve

A breakthrough curve [3] shown in Figure 3.1 is useful to explain this. C_0 is the contaminant concentration, C is the eluent concentration. With a steady flow rate, initially C is zero. Kinetic leakage starts just before breakthrough point (t_b), breakthrough concentration is C_b. After breakthrough point is reached, C/C_0 starts to increase rapidly, at total capacity loss point (t_t), C/C_0 becomes 1.

Fouling of resin decreases the number of available exchangeable sites for the incoming ions from the bulk solution. Bulky organic surfactants can also impede the ions to reach active sites hence reduce the rate of exchange. This reduces the exchange capacity of the resin which can result in a quick ion leakage and breakthrough point (t_b) at the operating flow rate. If the problem is not

addressed, more contaminant ions will be present in the feedwater causing serious damage. Due to fouling, the resin column needs replacement and regeneration of resins sooner than expected.

Condensate polishing ion exchange resins are used in power plants to remove traces of ionic impurities present in water. Fouled resins need to be replaced and regenerated much faster. The cost of 20% resin replacement per year can cost about 35-40% of the total annual operating cost of the plant excluding additional plant downtime loss.[4] Alongside the economic factor, the resin quality must be maintained to deal with impurities to prevent corrosion and leaks that can lead to accidents.[5]

Alkalizing / Filming Amines and Exchange Capacity:

Filming and alkalizing amines are among the organic foulant of ion exchange resins those can significantly affect resin properties such as lowering of effective exchange capacity.[6] Amines can occupy active sites in the cation exchange resins by chemical interaction shown in figure 3.2.

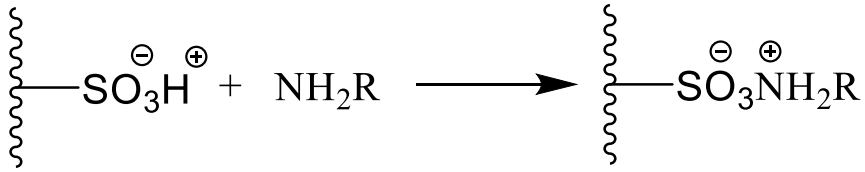

Figure 3.2: Ion exchange reaction of amines in cation exchange resin

Filming amines are surfactants with high affinity for surface, they can be adsorbed to the surfaces and polymer backbones of resins blocking access to the incoming ions.[7] That can also cause exchange capacity loss. The goal of this investigation is to determine how exchange capacity of

different resins are affected by interaction with different corrosion inhibitor amines. Exchange capacities were determined in standard, amine exposed and regenerated forms of resins.

Experimental:

Materials:

Interaction of three strong acid cation exchange resin and one strong base anion exchange resin with four alkalizing amines, four filming amines, and two commercial amines were studied.

Alkalizing amines:

1. Cyclohexylamine (Aldrich)
2. Ethanolamine (Alfa Aesar)
3. 4-methylmorpholine (Aldrich)
4. 5-amino-2-pentanol (Aldrich)

Filming amines:

1. Octylamine (Acros Organics)
2. Dodecylamine (Aldrich)
3. Octadecylamine (Alfa Aesar)
4. Oleylamine (Tokyo Chemical Indstries Co. Ltd.)

Commercial amines:

1. Anodamine
2. Cetamine (mixture of cyclohexylamine and (Z)-N-9-octadecenylpropane-1,3-diamine)

Ion exchange resins:

1. DOWEX 650C strong acid cation exchange resin
2. TCD-1 strong acid cation exchange resin
3. IRN-77 strong acid cation exchange resin
4. DOWEX 550A strong base anion exchange resin

Other reagents and their sources:

Hydrochloric acid (Pharmco Aaper), sodium hydroxide (EMD Chemicals Inc.), sodium chloride (Fisher Scientific Co.), standard 0.1 M hydrochloric acid (Alfa Aesar), isopropanol (Pharmco Aaper), methylene blue (Sigma – Aldrich), methyl red (Fisher Scientific Co.), deionized water (18 megaohms).

Converting Resins to Standard Forms:

At first, resins were converted to their standard forms. H^+ form of cation exchange resin is considered as its standard form. For anion exchange resin, the standard form is the OH^- form.[8] Cation exchange resins were treated with 2 M HCl to convert to standard H^+ form. 20 mL resin was taken in a gravity column and 500 mL 2 M HCl solution was added. A slow elution rate of 2 mL/min was set to ensure enough time for ion exchange. After all the acid solution was eluted, the column was washed with deionized water. To make sure that all the ions from the adhering water to the resin beads are removed, a conductometer was used, the resin in the column was washed until the conductivity of the eluent was found to be zero. The resins were collected, vacuum dried and stored.

A similar process was repeated using 250 mL of NaOH for converting anion exchange resins to standard OH^- form. Figure 3.3 shows the process of conversion of resins to their standard forms.

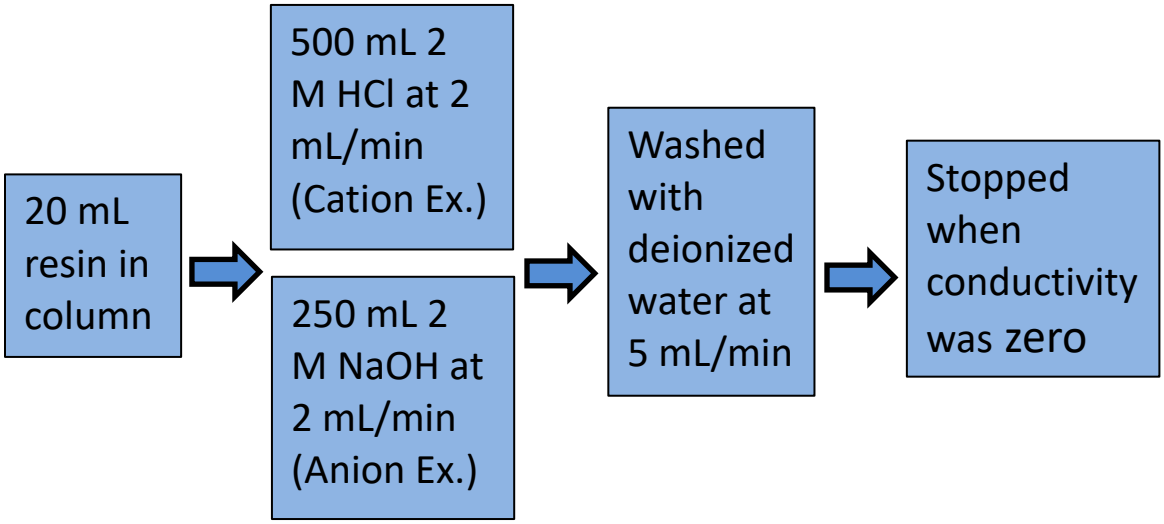

Figure 3.3: Conversion of resins to standard forms

Amine Solution Preparation and Exposing Resins:

0.1 M alkalizing amine solutions were prepared in deionized water, and 0.1 M filming amine solutions were prepared in isopropanol. 200 mL of alkalizing amine solutions were added to 10 mL of resins in a column to expose resins with amines and a slow flow rate of 1 mL/min was maintained.

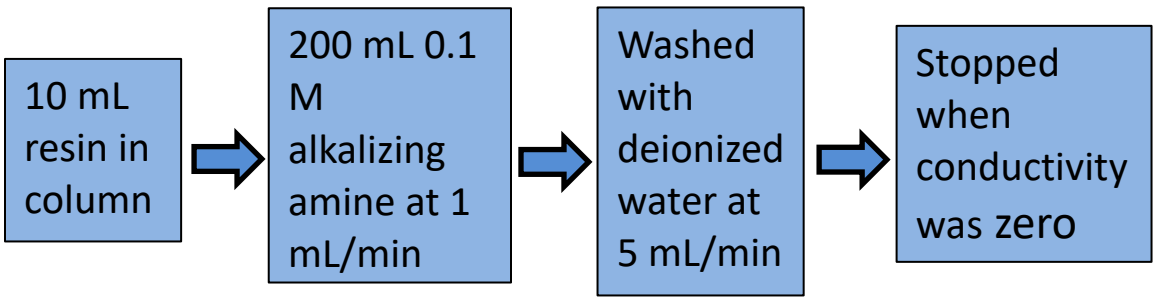

Figure 3.4: Exposing resins with alkalizing amines

After exposure, the resins in the column were washed using deionized water until the conductivity of the eluents were found to be zero. Figure 4.4 shows the process of exposing resins with alkalizing amines. Since filming amines are water insoluble, exposing resins required batch process. 200 mL of amine solutions were added to 10 mL of resins and mixed overnight to ensure maximum adsorption. The reins were filtered and washed with deionized water several times until the conductivity of the water after washing was found to be zero.

Regeneration after Amine Exposure:

Exposed resins were treated with 2 M HCl and 2 M NaOH for cation and anion exchange resins respectively to regenerate after amine exposure. The process was similar as conversion to standard forms. The purpose of regeneration was to replace any adsorbed amines by standard form ions.

Exchange Capacity Measurement / Calculation:

Exchange capacity is the measure of total monovalent exchangeable sites / ions present per liter or kilograms of resin. An easy way to measure is to calculate the total amount of hydrogen ions (H^+) present in cation exchange resin, or total hydroxide ions (OH^-) present in anion exchange resin. This can be done by adding sodium chloride (NaCl) solution to the resins in a column and titrating the collected eluent. H^+ ions in cation exchange resins will be replaced by Na^+ ions in the NaCl solution leaving an acidic (HCl) eluent that can be titrated against standard NaOH solution to find the exchange capacity. Similarly, anion exchange resins will leave a basic (NaOH) eluent since Cl^- ions in NaCl will knock off OH^- ions from the resin. The resulting basic solution can be titrated against standard HCl to calculate the exchange capacity of the anion exchange resin.

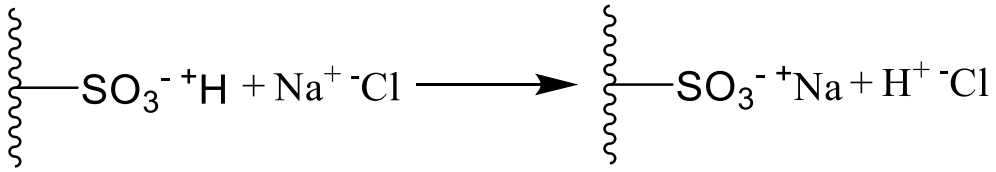

Figure 3.5: Reaction of NaCl with cation exchange resin

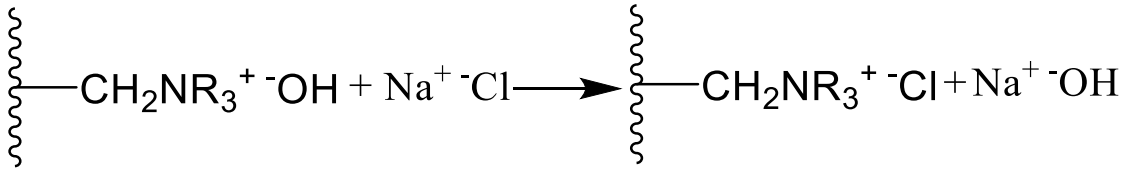

Figure 3.6: Reaction of NaCl with anion exchange resin

Amine exposed resins will release the remaining H^+ / OH^- ions since some of the exchangeable sites get exchanged / occupied by the exposure of amine.

Experimental Setup:

Column experiments are usually done for exchange capacity measurement. Use of more reagents and ion exchange resins, and being time consuming are among major drawbacks of column experiments, columns are also expensive. A simple experimental setup was made to make the process more efficient and easy.

Instead of regular columns, microcolumns were prepared using micropipettes. To maintain a slow flow rate, the outlets were narrowed using a Bunsen burner and only similar flow rate columns

were used to perform the experiments. Cotton tips were placed to restrict resins coming out of the columns or clogging the outlet.

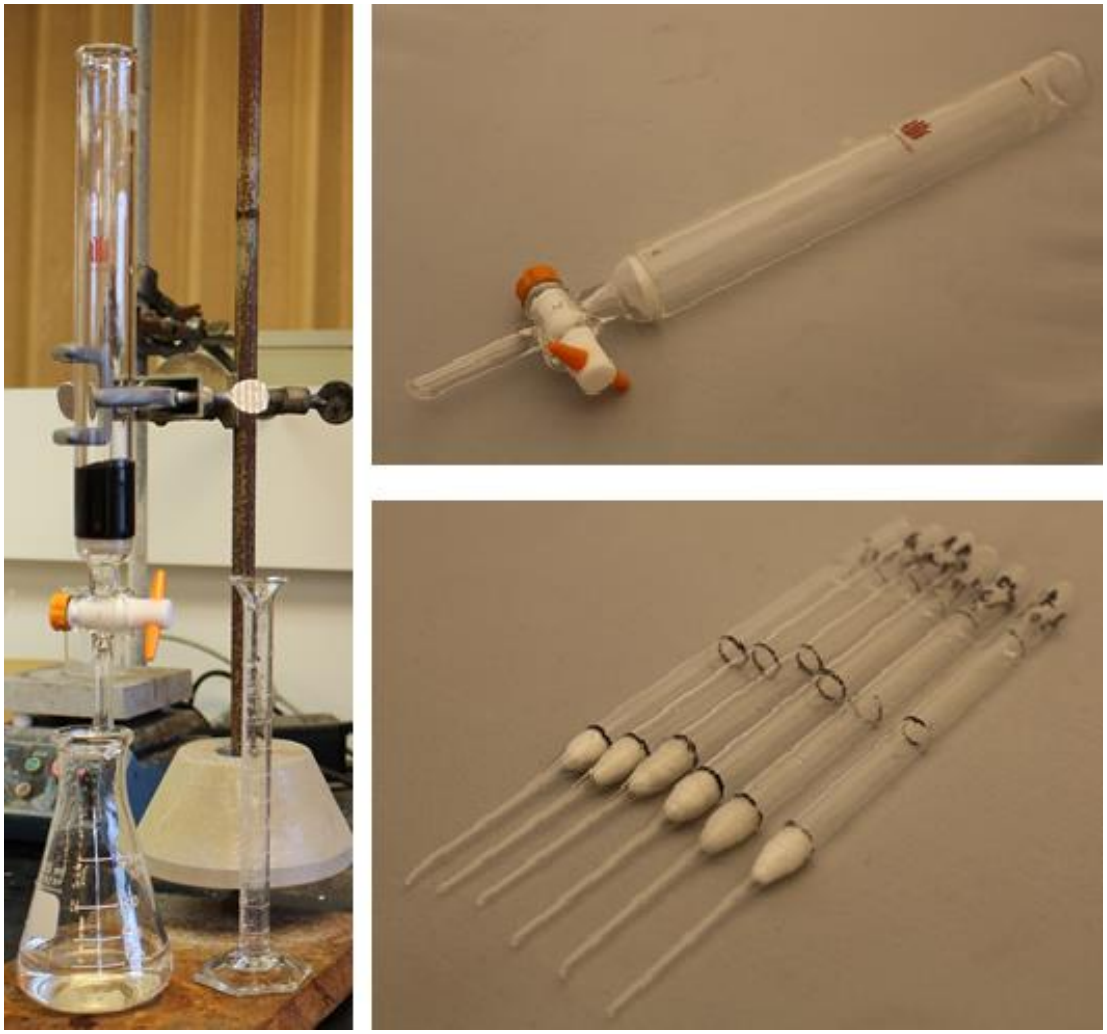

Figure 3.7: Regular columns and microcolumns

Use of microcolumns allowed use of only 1 mL of resin for each experiment, multiple columns were used at a time for doing several experiments simultaneously. Figure 3.8 shows the experimental setup of multiple microcolumns.

Figure 3.8: Microcolumn setup, and electronic burette used for titration

To 1 mL of resin, 20 mL of 5% NaCl solution (excess) was added slowly, the eluent was collected and titrated against standard 0.1 M NaOH (cation exchange resin) or 0.1 M HCl (anion exchange resin) using methylene blue – methyl red mixed indicator, an electronic burette was used for the titrations.

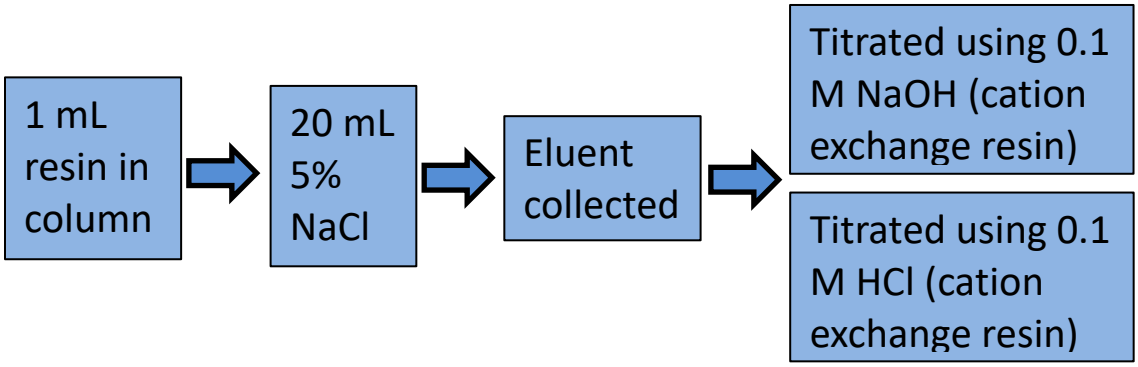

Figure 3.9: Exchange capacity experiment

The exchange capacities were calculated using the following equation:

$$\text{Exchange Capacity} = (0.1\ \text{M} \times \text{volume of NaOH or HCl in mL})\ \text{mol-eq/L}$$

Results and Discussion: Alkalizing Amines

Exchange capacity changes with cyclohexylamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	0.00	100
D650C regenerated		1.50	26
TCD-1 exposed	1.82	0.00	100
TCD-1 regenerated		1.31	28
IRN-77 exposed	1.97	0.00	100
IRN-77 regenerated		1.48	25
D550A exposed	1.03	0.99	4
D550A regenerated		0.99	4

Table 3.1: Exchange capacity and capacity loss, cyclohexylamine exposed and regenerated resins

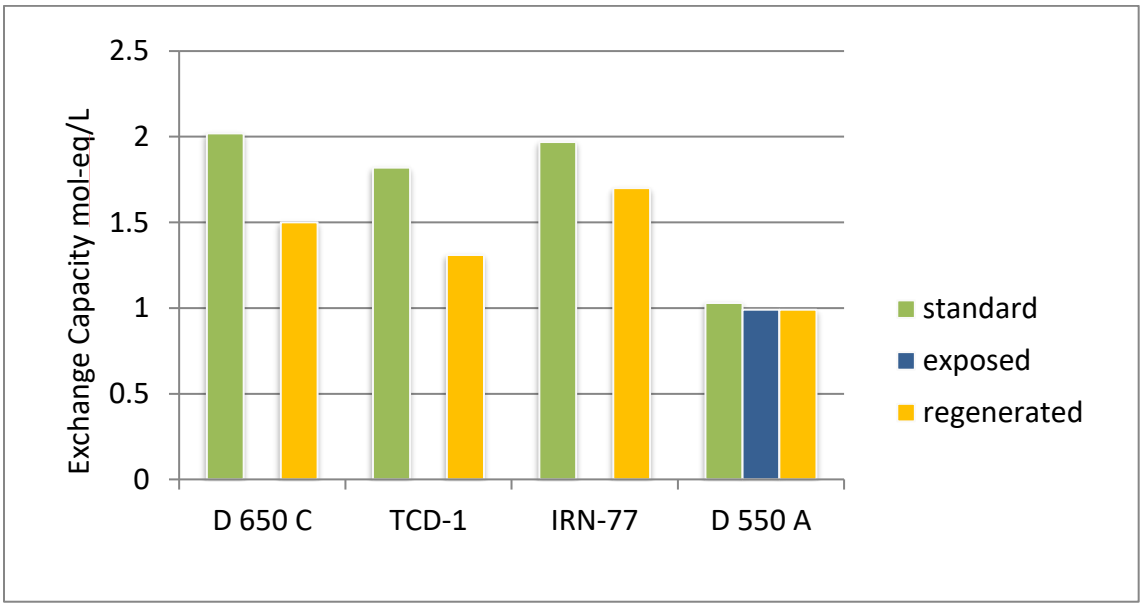

Figure 3.10: Exchange capacity comparison: Standard, cyclohexylamine exposed, and regenerated resins

Exchange capacity changes with 4-methylmorpholine exposure

Resins	**Standard**	**With Amine**	**% loss**
D650C exposed	2.02	0.00	100
D650C regenerated		1.48	27
TCD-1 exposed	1.82	0.00	100
TCD-1 regenerated		1.28	29
IRN-77 exposed	1.97	0.00	100
IRN-77 regenerated		1.40	29
D550A exposed	1.03	0.93	10
D550A regenerated		0.96	7

Table 3.2: Exchange capacity and capacity loss, 4-methylmorpholine exposed and regenerated resins

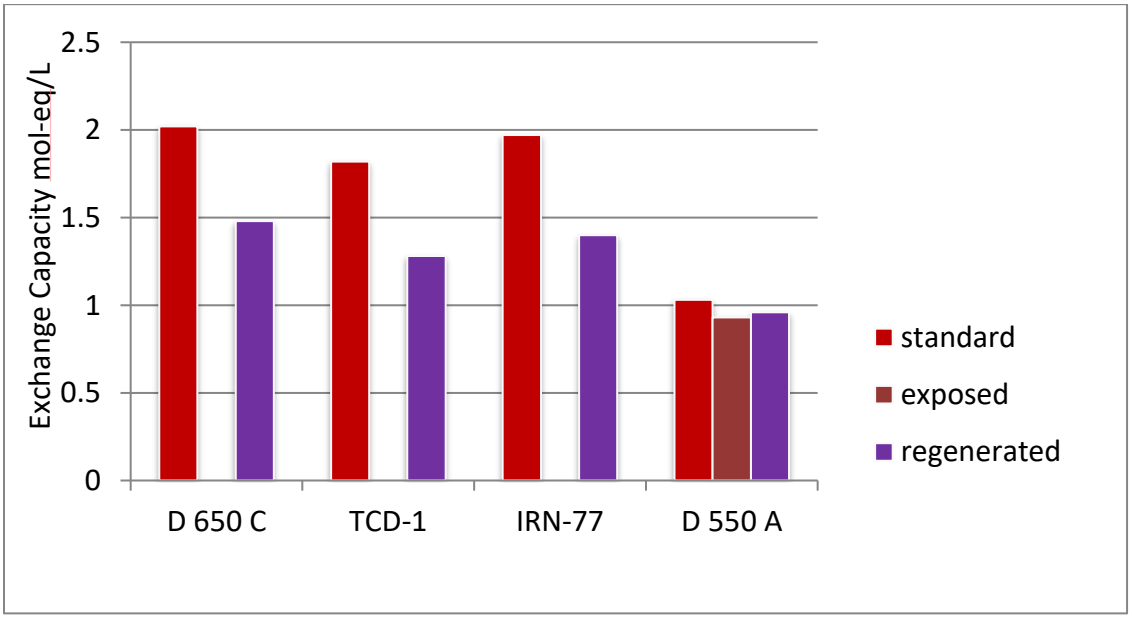

Figure 3.11: Exchange capacity comparison: Standard, 4-methylmorpholie exposed, and regenerated resins

Exchange capacity changes with ethanolamine exposure

Resins	**Standard**	**With Amine**	**% loss**
D650C exposed	2.02	0.0	100
D650C regenerated		1.55	23
TCD-1 exposed	1.82	0.0	100
TCD-1 regenerated		1.39	24
IRN-77 exposed	1.97	0.0	100
IRN-77 regenerated		1.49	24
D550A exposed	1.03	0.94	9
D550A regenerated		0.95	8

Table 3.3: Exchange capacity and capacity loss, ethanolamine exposed and regenerated resins

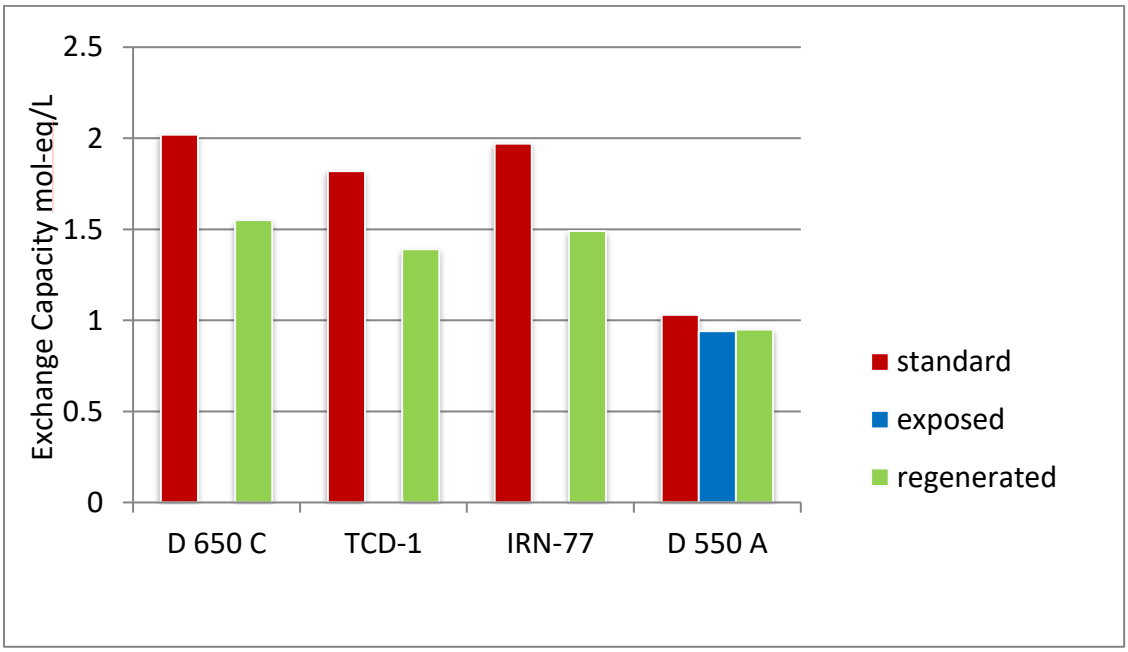

Figure 3.12: Exchange capacity comparison: Standard, ethanolamine exposed, and regenerated resins

Exchange capacity changes with 5-amino-2-pentanol exposure

Resins	**Standard**	**With Amine**	**% loss**
D650C exposed	2.02	0.0	100
D650C regenerated		1.62	20
TCD-1 exposed	1.82	0.0	100
TCD-1 regenerated		1.37	25
IRN-77 exposed	1.97	0.0	100
IRN-77 regenerated		1.47	25
D550A exposed	1.03	0.90	13
D550A regenerated		0.92	11

Table 3.4: Exchange capacity and capacity loss, 5-amino-2-pentanol exposed and regenerated resins

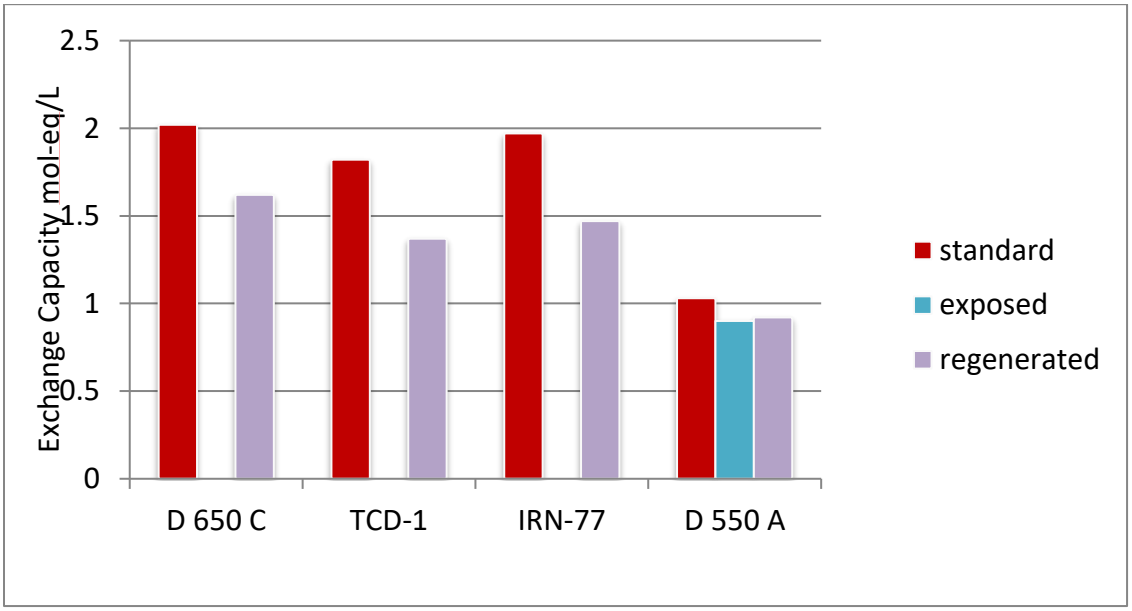

Figure 3.13: Exchange capacity comparison: Standard, 5-amino-2-pentanol exposed, and regenerated resins

Alkalizing Amine and Cation Exchange Resins:

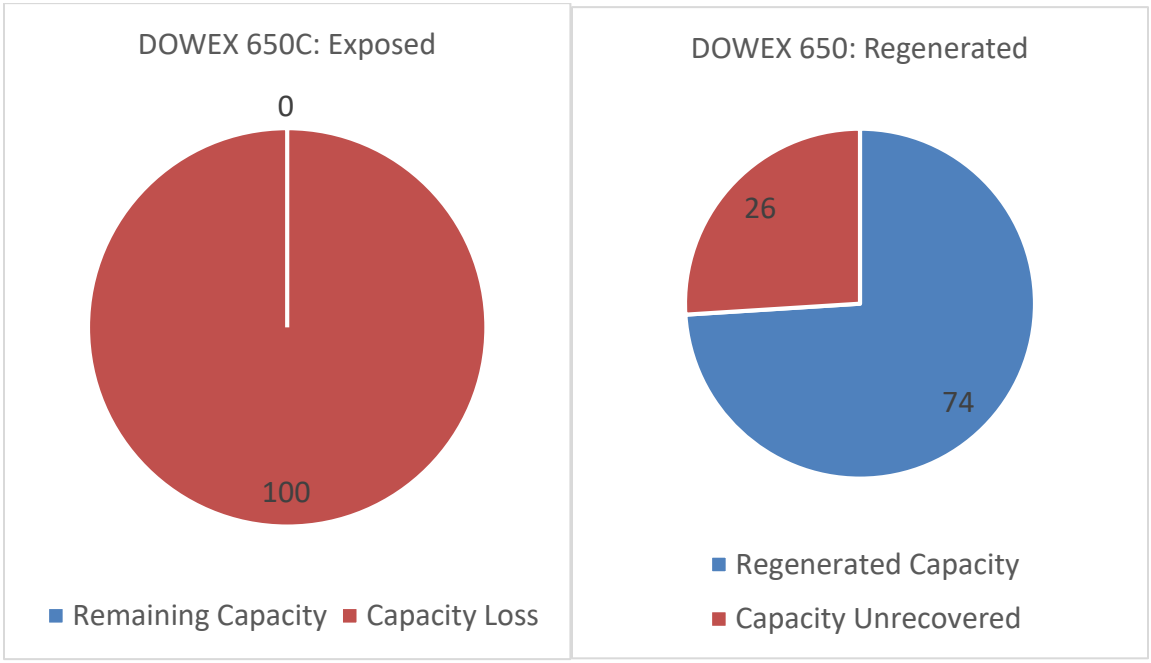

Figure 3.14: Exchange capacities of cyclohexylamine exposed and regenerated DOWEX 650C cation exchange resin

For all the cation exchange resins exposed with all the alkalizing amines, a 100% exchange capacity loss was observed. Amines exchanged all the exchangeable H^+ present in cation exchange resins and no HCl was produced when NaCl was added to the exposed resin. After regeneration, all the cation exchange resin exposed with different filming amines lost 20 to 30% of the original standard exchange capacity. A complete loss of DOWEX 650C exchange capacity is shown in figure 3.14 (left), after regeneration, 26% of the standard capacity was unrecovered. This inferred that the resins bound to the exchange sites did not exchange with H^+ during the regeneration process or the sites were completely blocked that did not allow H^+ reach the exchange sites.

Alkalizing Amines and Anion Exchange Resins:

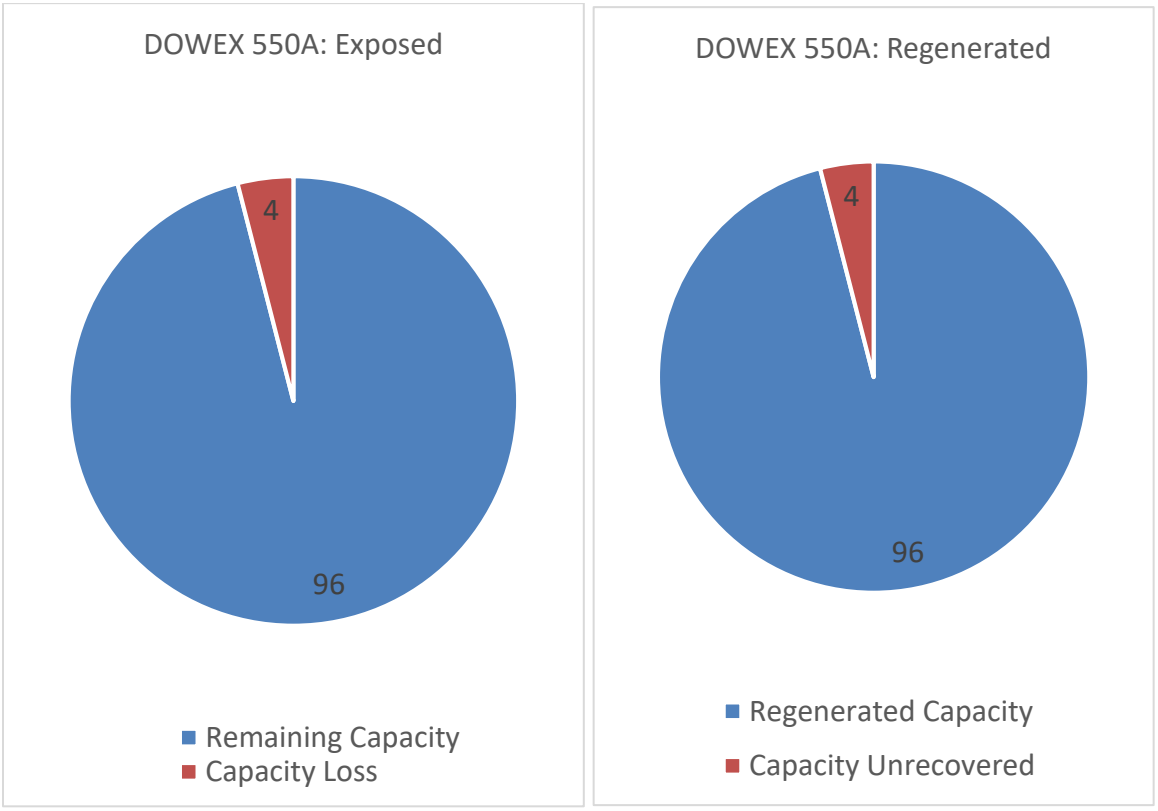

Figure 3.15: Exchange capacity of cyclohexylamine exposed and regenerated DOWEX 550A anion exchange resins

Exchange capacity loss was smaller (4-13%) when anion exchange resins were exposed to alkalizing amines. This was due to the fact that exchangeable sites in anion exchange resins are non-reactive to towards amines. Exchange capacity loss indicated adsorption of amines on the surface or polymeric backbone blocking the exchangeable sites. Most importantly, regenerated anion exchange resins showed a similar (4-11%) exchange capacity loss. The capacity lost during amine exposure were not recovered.

Results and Discussion: Filming Amines

Exchange capacity changes with octadecylamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	1.59	21
D650C regenerated		1.58	21
TCD-1 exposed	1.82	1.37	25
TCD-1 regenerated		1.57	14
IRN-77 exposed	1.97	1.33	32
IRN-77 regenerated		1.35	31
D550A exposed	1.03	0.93	10
D550A regenerated		0.95	8

Table 3.5: Exchange capacity and capacity loss, octadecylamine exposed and regenerated resins

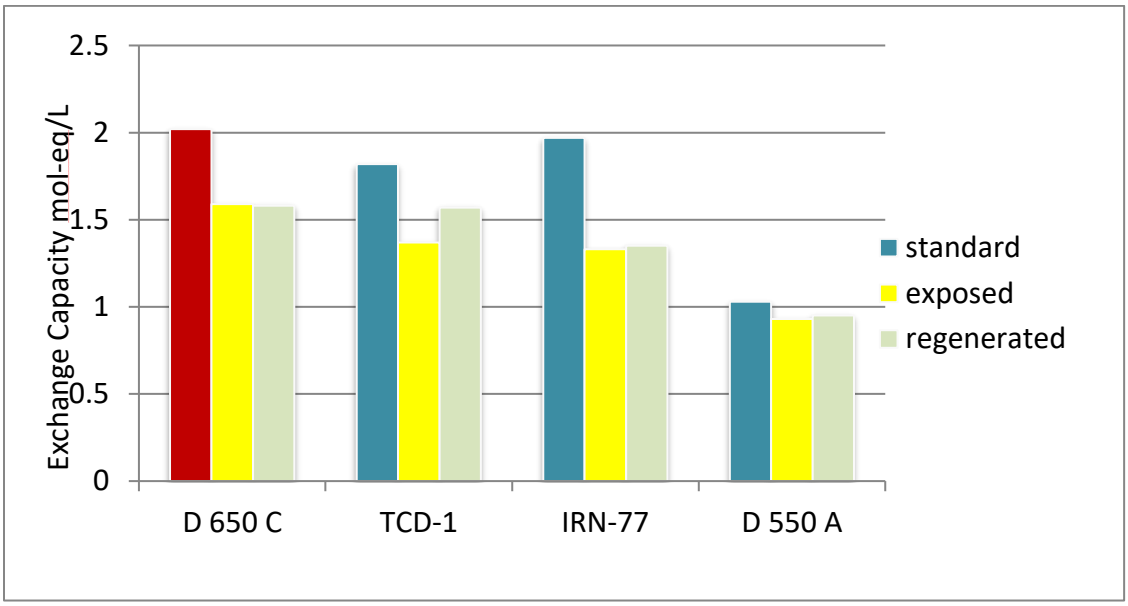

Figure 3.16: Exchange capacity comparison: Standard, octadecylamine exposed, and regenerated resins

Exchange capacity changes with dodecylamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	1.71	15
D650C regenerated		1.74	14
TCD-1 exposed	1.82	1.35	26
TCD-1 regenerated		1.31	28
IRN-77 exposed	1.97	1.36	31
IRN-77 regenerated		1.44	27
D550A exposed	1.03	0.70	32
D550A regenerated		0.71	31

Table 3.6: Exchange capacity and capacity loss, dodecylamine exposed and regenerated resins

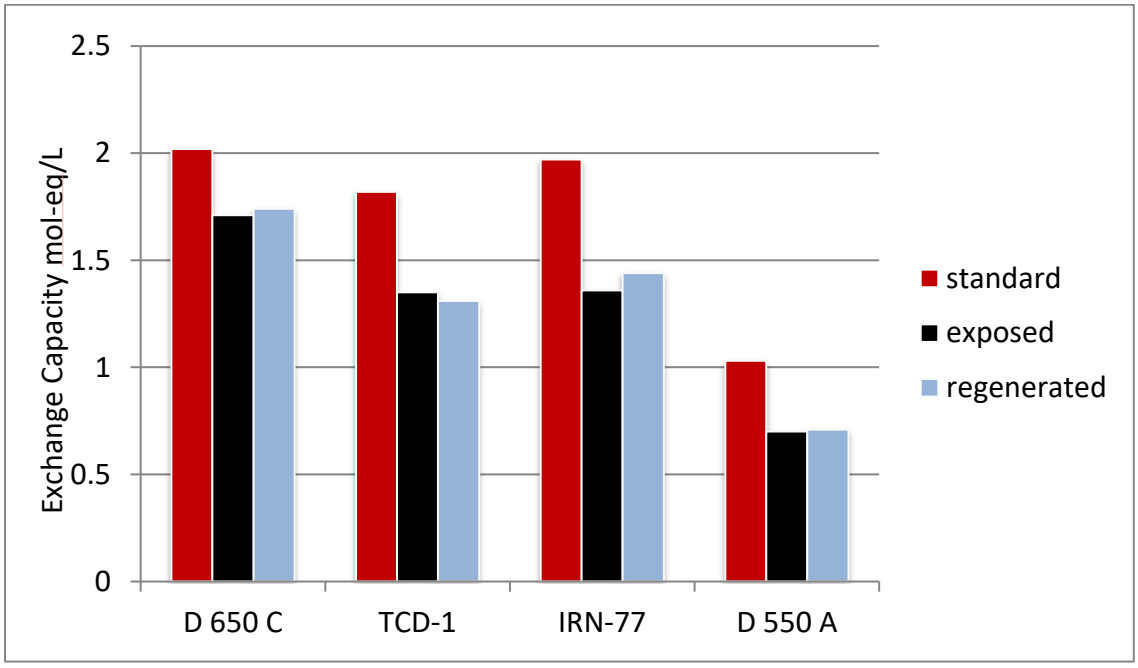

Figure 3.17: Exchange capacity comparison: Standard, dodecylamine exposed, and regenerated resins

Exchange capacity changes with oleylamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	0.0	100
D650C regenerated		1.05	48
TCD-1 exposed	1.82	0.03	98
TCD-1 regenerated		0.67	63
IRN-77 exposed	1.97	0.02	99
IRN-77 regenerated		0.87	56
D550A exposed	1.03	0.76	26
D550A regenerated		0.83	19

Table 3.7: Exchange capacity and capacity loss, oleylamine exposed and regenerated resins

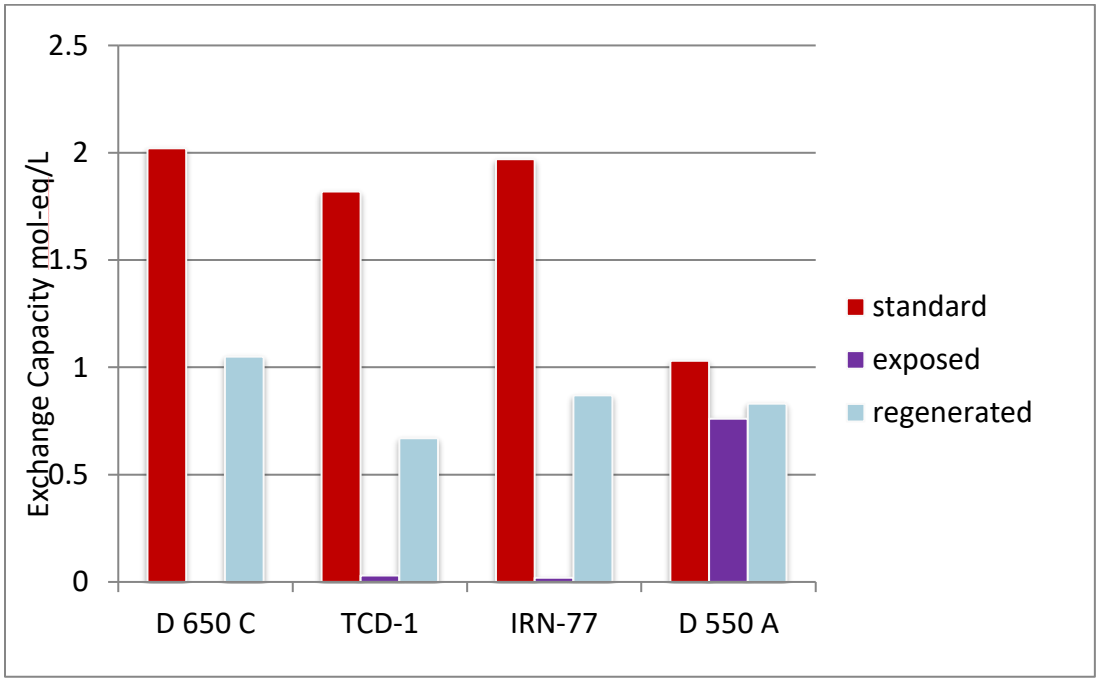

Figure 3.18: Exchange capacity comparison: Standard, oleylamine exposed, and regenerated resins

Exchange capacity changes with octylamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	0.0	100
D650C regenerated		0.38	81
TCD-1 exposed	1.82	0.0	100
TCD-1 regenerated		0.31	83
IRN-77 exposed	1.97	0.0	100
IRN-77 regenerated		0.34	83
D550A exposed	1.03	0.73	29
D550A regenerated		0.84	18

Table 3.8: Exchange capacity and capacity loss, octylamine exposed and regenerated resins

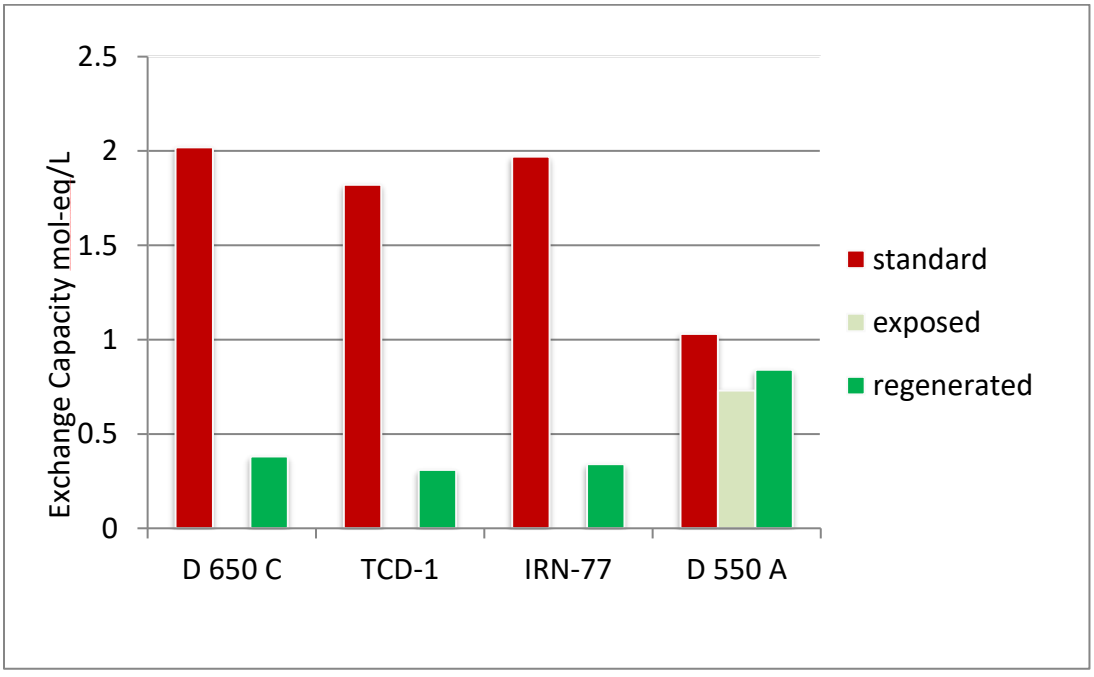

Figure 3.19: Exchange capacity comparison: Standard, octylamine exposed, and regenerated resins

Filming Amines and Cation Exchange Resin Exchange Capacity:

Filming amines are different than alkalizing amines due to their longer chain, hydrophobicity, and high affinity towards surface. Among the four filming amines studied: octylamine, dodecylamine, and octadecylamine have increasing chain lengths. Oleylamine is different than others since the structure is nonlinear due to presence of a double bond. The exchange capacity loss comparison of different filming amine exposed and regenerated DOWEX 650C cation exchange resin is shown in figure 3.20.

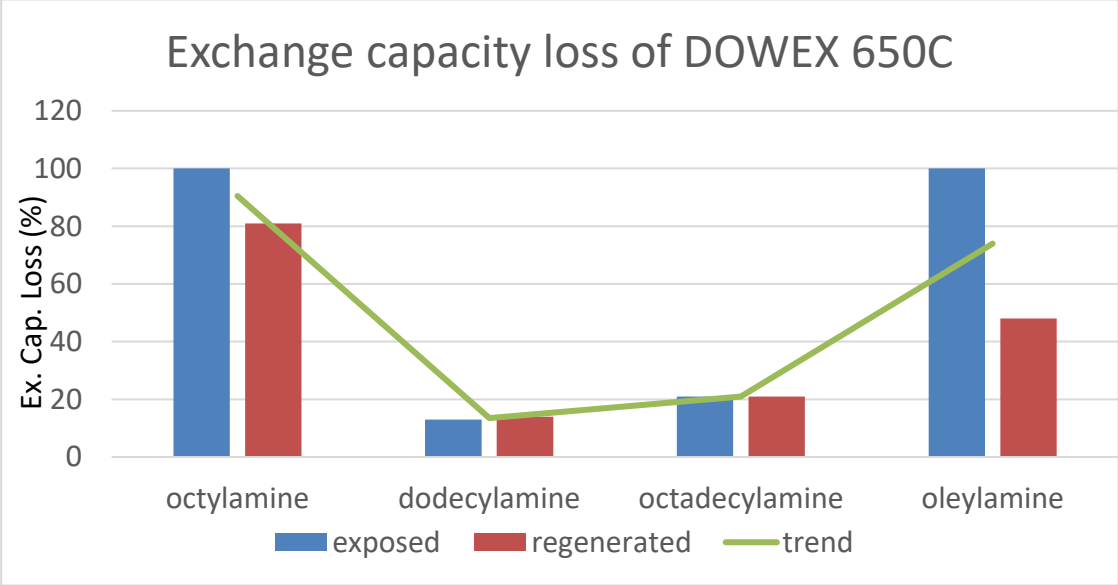

Figure 3.20: Exchange capacity loss of DOWEX 650C due to filming amine exposure

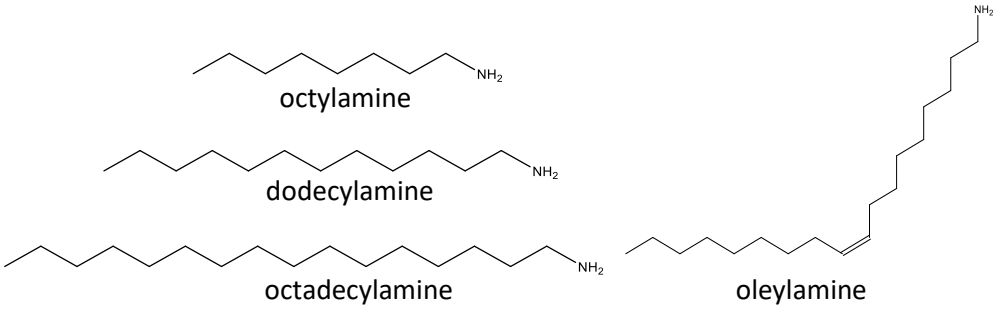

Figure 3.21: Filming amines

Octylamine, the shortest linear filming amine exposure caused a 100% exchange capacity loss, while exchange capacity loss for a longer chain dodecylamine exposure was found to be only 15%. Chain length must have played an important role for this significant difference. Ion exchange resins are functionalized cross linked polymers that contain exchangeable groups on the resin bead surface and inner matrix as well. A longer chain, larger size amine finds it difficult to enter the matrix hence dodecylamine had a smaller exchange capacity loss compared to octylamine.

Moving to octadecylamie, longest of the linear filming amines, a higher capacity loss (21%) was observed compared to dodecylamine. Hydrophobicity and surface affinity increases with increasing size. Filming amines make it harder for ions in the solution to reach the exchangeable sites by occupying surface, and their hydrophobicity also resists the ionic hydrophilic species. 100% exchange capacity loss was observed for oleylamine exposed resin which similar as of octylamine.

Exchange capacity of regenerated DOWEX 650C after exposing with octylamine was found to be 0.38 mol-eq/L which was only 19% of the standard resin. 81% exchange capacity was lost, most of the exchangeable sites were either occupied or H^+ could not reach during regeneration process. Apparently, fouling was most severe in this case since lowest exchange capacity was observed after regeneration. 48% exchange capacity loss was found for oleylamine regenerated DOWEX 650C.

Though higher exchange capacities were found for dodecylamine and octadecylamine regenerated DOWEX 650C, regeneration was completely ineffective. Once bound to the active sites of on the surface, these filming amines permanently occupied those areas. Similar trends were found for TCD-1 and IRN 77 cation exchange resins due to exposure with different filming amines. Octylamine can penetrate the cation exchange resin matrix but dodecylamine and longer

linear chain filming amines must be too big. Regeneration is very poor for all filming amines and it becomes difficult to regenerate exchange capacity with increasing chain length.

Filming Amines and Anion Exchange Resin Exchange Capacity:

Exchange capacity loss of DOWEX 550A anion exchange resin due to different filming amine exposure is shown in figure 3.22. Compared to alkalizing amines, effect on exchange capacity were much greater when exposed to filming amines. This was due to higher hydrophobicity, and surface affinity.

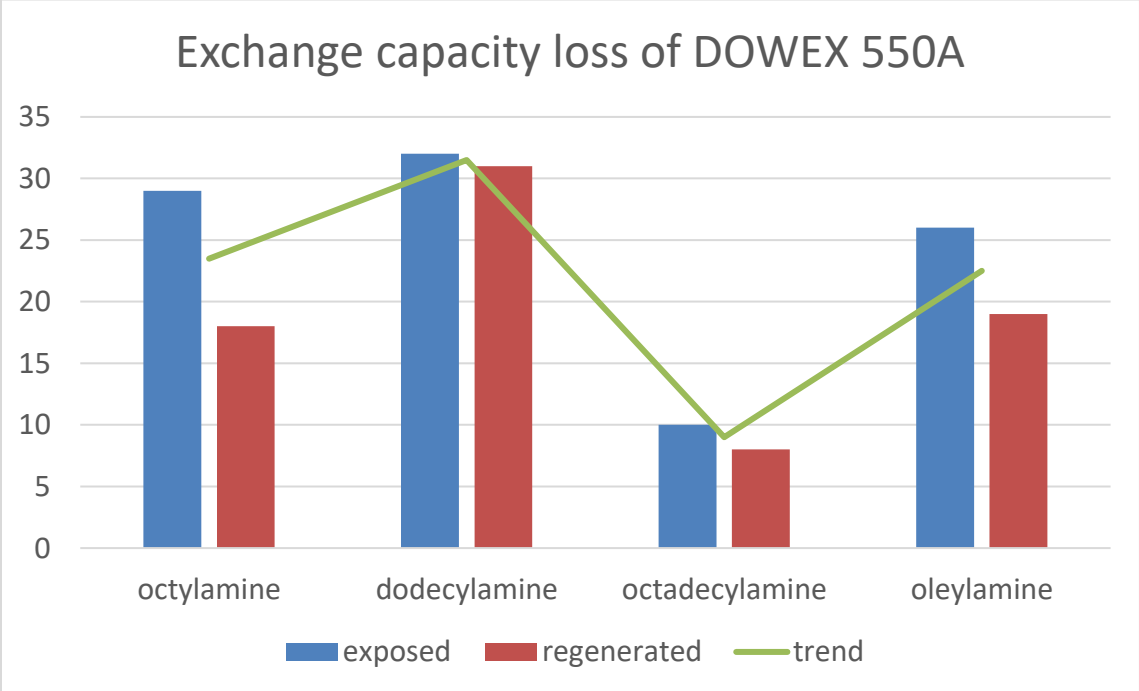

Figure 3.22: Exchange capacity loss of DOWEX 550A due to filming amine exposure

For anion exchange resin, dodecylamine exposure was found to have highest effect on exchange capacity with a 32% loss. 29% exchange capacity was found for exposed resin octylamine, that was similar as dodecylamine. Octadecylamine exposed resin showed a significantly lower (10%) exchange capacity loss compared to dodecylamine. Density of DOWEX 550A is lower (657 g/L) than cation exchange resins (DOWEX 650C, 785 g/L) and swelling is higher (25%).[9-10] This resulted in larger pores within anion exchange resin matrix that allowed filming amines with chain length of dodecylamine and lower to penetrate, but octadecylamine was too big. For cation exchange resins, due less swelling and smaller pore size, dodecylamine and higher chain length filming amines could not access the resin matrix. Oleylamine exposed resin behaved similar as octylamine. Regeneration was found difficult for dodecylamine and octadecylamine. Due to smaller size, octylamine showed better regeneration, but for all the filming amines, complete regeneration was not achieved.

Results and Discussion: Commercial Amines

Two commercial amines, Anodamine and Cetamine were received from Electric Power Research Institute (EPRI). The composition of Anodamine was unknown, Cetamine contained cyclohexylamine as alkalizing agent and (Z)-N-9-octadecenylpropane-1,3-diamine as filming amine. Due to small amount of sample provided, a 10 fold diluted Anodamine solution was added to expose resins.

Exchange capacity changes with Anodamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	1.59	21
D650C regenerated		1.89	7
TCD-1 exposed	1.82	1.45	20
TCD-1 regenerated		1.78	5
D550A exposed	1.03	0.79	23
D550A regenerated		1.01	2

Table 3.9: Exchange capacity and capacity loss, Anodamine exposed and regenerated resins

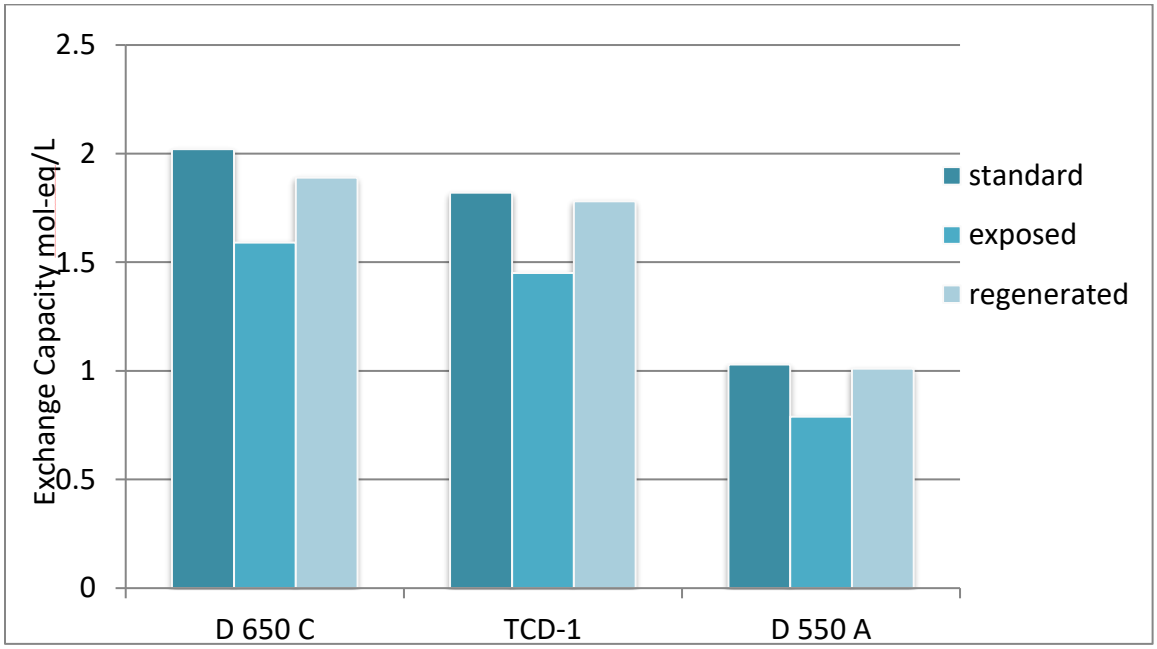

Figure 3.23: Exchange capacity comparison: Standard, Anodamine exposed, and regenerated resins

Exchange capacity changes with Cetamine exposure

Resins	Standard	With Amine	% loss
D650C exposed	2.02	0.0	100
D650C regenerated		1.91	5
TCD-1 exposed	1.82	0.0	100
TCD-1 regenerated		1.71	6
D550A exposed	1.03	1.02	1
D550A regenerated		1.02	1

Table 3.10: Exchange capacity and capacity loss, Cetamine exposed and regenerated resins

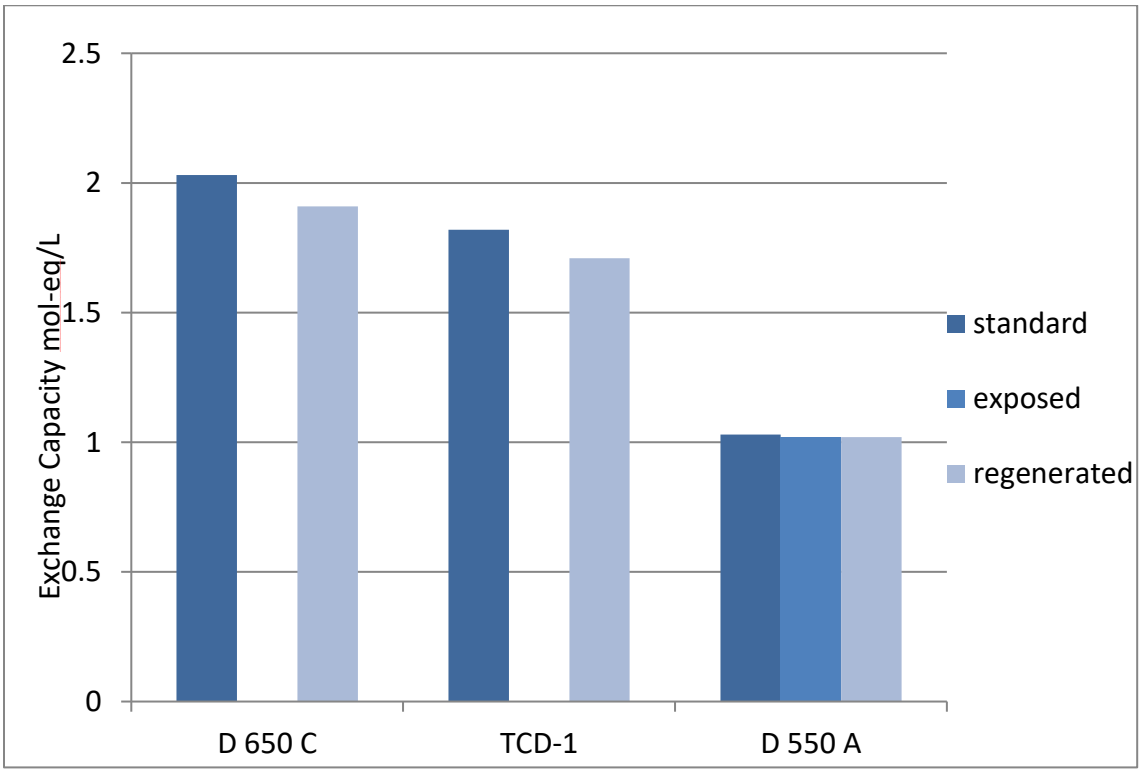

Figure 3.24: Exchange capacity comparison: Standard, Anodamine exposed, and regenerated resins

Commercial Amines and Resin Exchange Capacities:

Diluted Anodamine exposed cation exchange resin exchange capacities were reduced by 20%. Since the concentration of amine was low, the exchangeable sites were not saturated. Cetamine exposed cation exchange resin capacities were completely lost after exposure. In both cases, regeneration was better for commercial filming amines as compared to alkalizing and filming amines used for previously described experiments. The capacity loss for cation exchange resins were found to be 5-8%. Anion exchange resins were almost unaffected by exposure to commercial amines.

Resin Structure, Amine Size and Hydrophobicity:

All the resins used for the experiments are gel type microporous resins with a pore size of 1-2 nm. Figure 3.25 shows the pore structure of a gel type resin.[11]

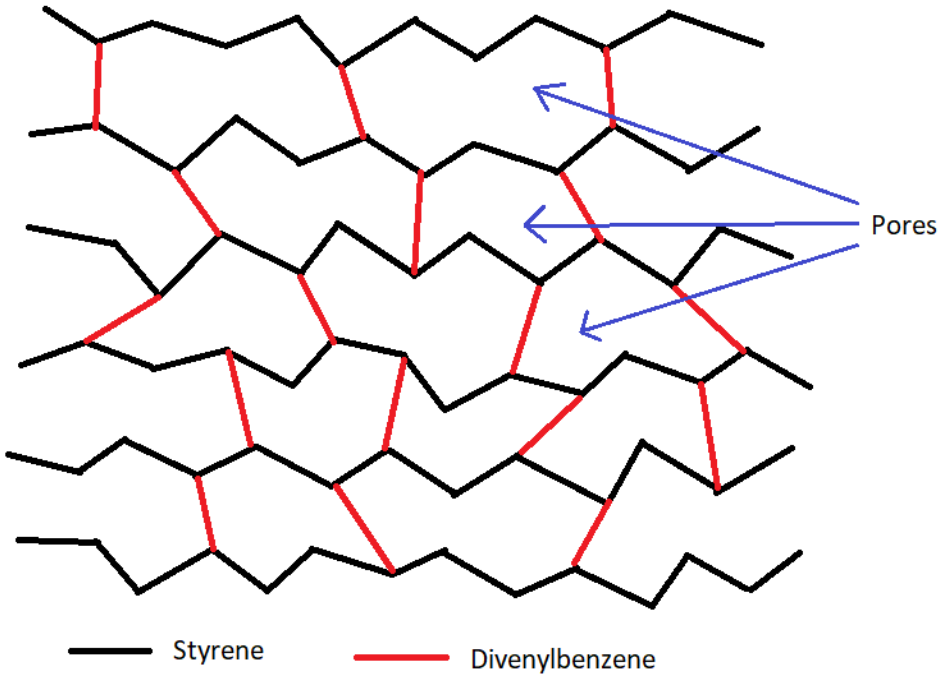

Figure 3.25: Gel type resin pore structure [11]

Amines about the size of octylamine (~ 1.1 nm) fit in the cation exchange resin pores and completely occupy ion exchange sites. Octylamine had the most negative impact on cation exchange resin performance. For anion exchange resins, dodecylamine (~ 1.6 nm) and smaller size amines can fit easily. With increasing size and hydrophobicity, removal during regeneration is lower, and permanent resin fouling occurs to a greater extent. Larger amines that do not fit in the pores foul the surface of the resin beads. The most damaging amines are the considerably hydrophobic ones that fit snugly into the resin pores.

Conclusion:

Both cation and anion exchange resins can be fouled by alkalizing and filming amines. It was found that 20-29% exchange capacity was lost after regeneration for alkalizing amine exposure. 4-methylmorpholine was most damaging towards cation exchange resins. 4-13% exchange capacity loss was found for anion exchange regenerated resins. 5-amino-2-pentanol was found to be most damaging towards DOWEX 550A. This can lead to serious problem since the water purification system will reach breakthrough point much faster at a regular flow rate when regenerated resins will be used. This is more problematic for cation exchange resins since regeneration is relatively poor.

Filming amines cause greater damage to the exchange capacity that increase with increasing size, hydrophobicity, and affinity for surface. Octylamine had most negative effect on cation exchange resins since it could fit in the pores and made the matrix hydrophobic. For anion exchange resin, dodecylamine was most damaging. Both cation and anion exchange resins are heavily fouled by filming amines and very poor regeneration severely affect the exchange capacity.

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11. http://dardel.info/IX/resin_structure.html. **accessed June 2017**.

CHAPTER IV

EFFECT OF FILMING AND ALKALIZING AMINES ON RESIN PROPERTIES

Introduction

Besides exchange capacity, other important resin properties are:[1]

- Appearance and color of resin
- Apparent density
- Moisture content
- Bead size and shape

Ion exchange resins are functionalized cross-linked polymers of polystyrene and divinylbenzene. Resin bead appearance and color depends on the functional groups and exchangeable ions present in it. Cation exchange resins can show a wide range of colors due to presence of different metal ions attached to them.[2] Organic dyes are introduced to some of the resins during synthetic process that acts as acid-base indicator.[3] A long storage time can lead to formation of degradation products that can also cause a color change in resins.[4]

Exposing with amines can change resin appearance and color, especially for cation exchange resins, since chemical reactions take place and the exchangeable groups are replaced. Moreover, the amines are basic in nature, resins with acid-base indicators can show a direct color change of the indicator.

Figure 4.1: Different commercially available resins

The degree of crosslinking determines the resins mechanical stability and the ability to expand when put in water.[5] Expansion of resin beads by absorbing water is known as swelling. The swelling process is shown in Figure 4.2.

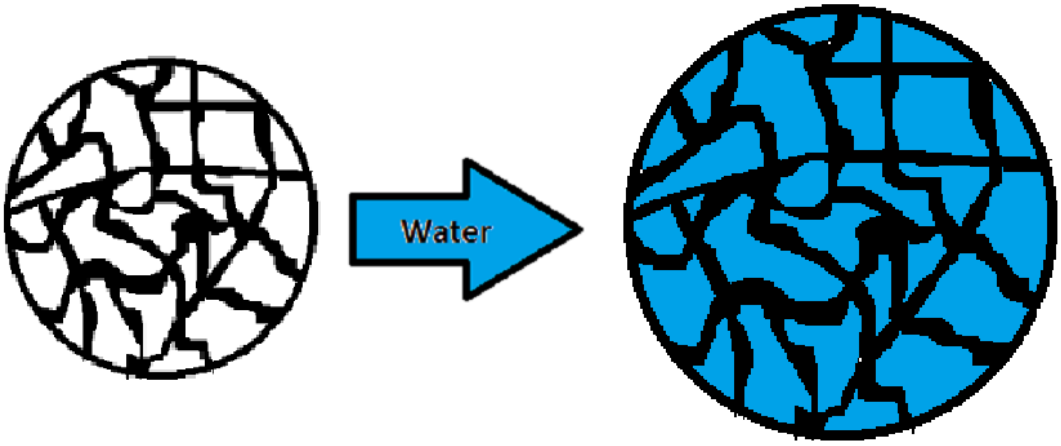

Figure 4.2: Swelling of resin bead

When resins are allowed to swell in water completely, and water from the surface is removed, apparent density is the density of swelled resins. Moisture content is the total water content of the resin at completely swelled form. It can also be expressed as amount of water loss by swelled resin when completely dried. Resin beads are spherical with varying sizes depending on type of resin.

These resin properties can be affected by the exposure of alkalizing and filming amines, especially filming amines. Hydrophobic and water insoluble amines can resist water to get into the resin matrix, hence reduce swelling, that can affect apparent density and moisture content. Permanent blocking of active sites and surfaces can potentially damage the resin beads too.

Effect of Amine Exposure on Appearance and Color of Resins:

Color changes in cation exchange resins were observed during the process of exposing and also regeneration of resins with different amines. Amines are weak bases; hence the changes were easily seen for TCD-1 that contains an acid-base indicator. The standard H^+ form of TCD-1 had a bright purple color that completely turned yellow after exposing with all the filming amines. After regeneration, the purple color reappeared.

As described in the previous chapter, the exchange capacities of cation exchange resins were completely lost by the exposure of all alkalizing amines. Around 75% exchange capacity was restored by the process of regeneration. These results are coherent. Due to complete exchange of alkalizing amines for H^+ in the cation exchange resins, the color changed from purple to yellow indicating basic nature of the resin by alkalizing amine exposure. After regeneration, most of the exchangeable sites were H^+, the overall acidic nature of the resin was indicated by purple color.

DOWEX 650C and IRN77 also showed a slight change. The exposed resins were found to be lighter in color compared to the standard and regenerated resins. The color change comparison for 4-methylmorpholine and ethanolamine exposed and regenerated cation exchange resins are shown in Figure 4.3 and 4.4.

Figure 4.3: Difference in color, 4-methylmorpholine exposed (left) and regenerated (right) resins.

DOWEX 650C (1), TCD-1 (2), IRN77 (3)

Figure 4.4: Difference in color, ethanolamine exposed (left) and regenerated (right) resins.

DOWEX 650C (1), TCD-1 (2), IRN77 (3)

A different pattern of color change was observed for filming amine exposed and regenerated cation exchange resins. Octadecylamine and dodecylamine exposed TCD-1 resins were light purple compared to standard resins and the regenerated resins also showed similar color. The color changes in other cation exchange resins were not very significant. Octadecylamine and dodecylamine exposed cation exchange resin exchange capacity losses were around 20%, that left more H^+ unexchanged making the resin acidic. Regeneration was found to be very poor, 20% exchange capacity loss was not recovered.

The same trend was observed in color change and exchange capacity loss for relatively longer chain filming amine exposed and regenerated resins. Due to longer chain, higher hydrophobicity and surface affinity, these filming amines could not interact easily within the matrix, and regeneration did not work. Figure 4.5 shows color change in different cation exchange resins due to dodecylamine exposure and regeneration.

Figure 4.5: Difference in color, dodecylamine exposed (left) and regenerated (right) resins.

DOWEX 650C (1), TCD-1 (2), IRN77 (3)

Shorter chain octylamine, and bent oleylamine showed a different pattern. Both exposed and regenerated TCD-1 had yellow color, not as bright as alkalizing amine exposed resin. Filming amines are hydrophobic and less basic compared to alkalizing amines, that might be the reason for a different color. The exchange capacity loss of cation exchange resins was 100% for exposing with both amines. Regeneration recovered only 20% for octylamine exposed and less than 50% for oleylamine exposed cation exchange resins leaving them basic in nature. Figure 5.6 shows color change in different cation exchange resins due to octylamine exposure and regeneration.

Figure 4.6: Difference in color, oleylamine exposed (left) and regenerated (right) resins.

DOWEX 650C (1), TCD-1 (2), IRN77 (3)

Apparent Density and Moisture Content:

To calculate apparent density and moisture content, resin was put in deionized water for few minutes to ensure complete swelling. A moisture balance, Metler Toledo HR73 halogen moisture analyzer, was used for the experiments.

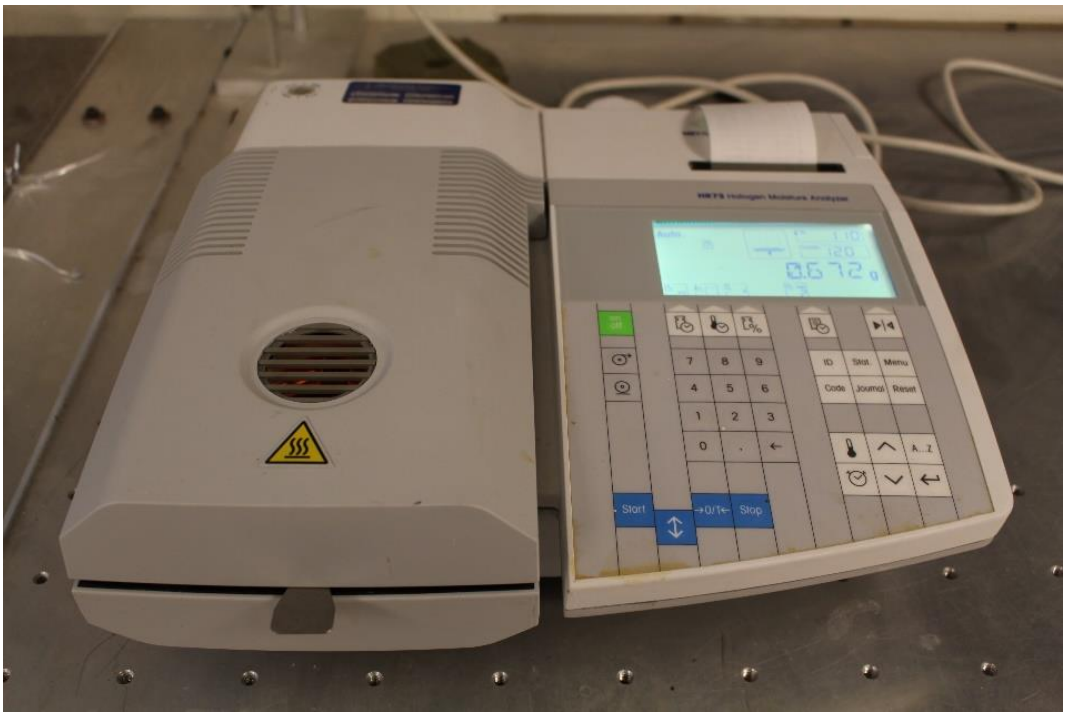

Figure 4.7: Metler Toledo HR73 halogen moisture analyzer

1 mL completely swelled resin was measured and vacuum filtered for few minutes to remove surface water. It was placed on an aluminum dish and put into the moisture balance. The apparent density was calculated from the initial mass using the following equation.

$$\text{Apparent Density} = \text{Wet Resin Mass X } 1000 \text{ (g/L)}$$

The moisture analyzer temperature was set at 110º C and it recorded resin mass at 2 minute intervals. When all the water absorbed by the resin was evaporated, a steady mass was reached. The moisture content was calculated as:

$$\text{Moisture Content} = \left(\frac{\text{Mass loss}}{\text{Initial mass}}\right) \text{X } 100\ \%$$

Effect of Alkalizing and Filming Amines on Moisture Content of Ion Exchange Resins:

Both alkalizing and filming amines were found to affect apparent density and moisture content of cation exchange resins. The table below shows results for cyclohexylamine and octylamine exposed, and regenerated DOWEX 650C cation exchange resin.

Amine used	**Apparent density (g/L)**	**Moisture content (%)**
None (Standard resin)	739	47
Cyclohexylamine exposed	671	21
Cyclohexylamine regenerated	711	42
Octylamine exposed	678	15
Octylamine regenerated	670	17

Table 4.1: Apparent density and moisture content of DOWEX 650C, cyclohexylamine and octylamine, exposed and regenerated

Apparent density calculations are subject to high error. Moreover, filming amines were dissolved in isopropanol, that could replace some water within the resin beads. But overall, lower apparent densities were found for all the forms of resin compared to standard resin. Amines have lower density compared to water, remaining amines in the resin matrix can be the reason for observed lower apparent densities.

Moisture contents were lowered significantly for both alkalizing and filming amine exposed resin. Amines are larger in size compared to H^+, that occupied the pores and resisted water absorption during the swelling process. Alkalizing amine regenerated cation exchange resin moisture contents were almost completely restored, but regeneration did not improve filming amine regenerated cation exchange resin moisture content. Water soluble, smaller size alkalizing amines were easily regenerated but hydrophobic long chain filming amines stayed blocking the active sites, pores and also surfaces.

Apparent densities of alkalizing and filming amine exposed and regenerated resins were also found to be lower compared to the standard form resins. Cyclohexylamine and octylamine exposed and regenerated DOWEX 550C anion exchange resin results are shown in Table 4.2.

Amine used	**Apparent density (g/L)**	**Moisture content (%)**
None (Standard resin)	636	65
Cyclohexylamine exposed	615	62
Cyclohexylamine regenerated	595	66
Octylamine exposed	484	12
Octylamine regenerated	530	13

Table 4.2: Apparent density and moisture content of DOWEX 550A, cyclohexylamine and octylamine, exposed and regenerated

Alkalizing amines did not affect moisture contents of anion exchange resins. A significant moisture content loss was observed for filming amine exposed anion exchange resins and regeneration was not successful. This resulted in due to larger size and hydrophobicity of filming amines, also use of isopropanol as solvent at the time of exposing.

Size and Shape:

Scanning electron microscopy (SEM) images were taken to see the change in size and shape. Figure 4.8 shows images of standard and Cetamine exposed DOWEX 650C.

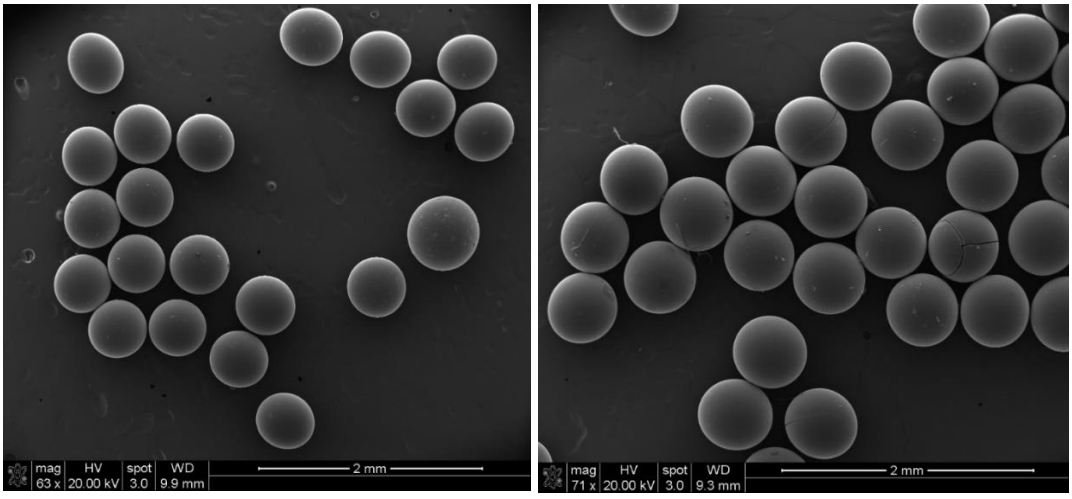

Figure 4.8: SEM images of standard (left) and Cetamine (right) exposed DOWEX 650C

Average size of Cetamine exposed resin beads was found to be slightly bigger compared to standard H^+ form resin. This could be due to adsorption of amines present in Cetamine. More cracked beads were also observed after exposure, that suggests filming amines can be responsible for structural damage of the resin beads.

Discussion:

Cation exchange resin color changes were observed due to alkalizing and filming amine exposure. TCD-1 cation exchange resin containing acid base indicator best showed the changes. The color change observations were also consistent with the exchange capacity loss results described in the previous chapter. Alkalizing amines exchanged all the H^+ present and the color indicated presence of base. This supports 100% exchange capacity loss of cation exchange resins by the exposure of alkalizing amines observed in Chapter 2. After regeneration, most of the H^+ (70-80% exchange capacity was recovered) were restored and we observed that the original color of TCD-1 reappeared. Filming amines those can fit in the resin matrix, also changed the color to basic. Regeneration could not restore active H^+sites, and the color did not change back to the original. Larger filming amines such as dodecylamine and octadecylamine, those could not go into the pores slightly changed the color, and after regeneration the color change stayed indicating unsuccessful regeneration. In Chapter 2, we found that approximately 20% exchange capacity was lost and regeneration could not recover that.

Apparent density and moisture content was also affected. For all exposed and regenerated resins, a reduced apparent density was found. Alkalizing amines lowered moisture content of cation exchange resins only but it was restored close to the standard value after regeneration. Filming amines affected moisture content of both anion and cation exchange resins severely, regenerated resins also had similar moisture content as exposed resins. Hydrophobic long chain filming amines permanently occupied pores and surfaces, use of isopropanol as a solvent for filming amines may also have played a role.

Filming amines also have the potential to cause structural damage and resin breaking, further studies required to show more evidences.

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CHAPTER V

UPTAKE OF AMINES BY ION EXCHANGE RESINS: EVIDENCES OF RESIN FOULING

Fouling of Ion Exchange Resins:

Contaminants such as organic foulants in feedwater, thermal degradation, incomplete separation or regeneration can foul ion exchange resins.[1] The fouling process can be broadly divided into two categories: loss of ion exchange site activity and fouling of non-ion change polymeric backbone. Fouling of non-ion exchange areas can increase the physical resistance to ionic species in the bulk solution to reach the ion exchange sites. Cation exchange resin fouling can occur by adsorption of suspended species those are produced due to precipitation when there is a pH change. Adsorption of ions those are hard to be removed by normal regeneration can cause fouling.[2] Iron oxides complexed with organics can accumulate and gradually degrade the cation exchange resin. Anion exchange resins can be fouled in similar fashion. The quality of anion resin can be degraded by replacement of Ion exchange site by ionic species of higher functionality.[3]

Amines and Condensate Polisher Resin Fouling:

Alkalizing and filming amines are used in condensate systems as corrosion inhibitors. Alkalizing amines are short chain, water soluble, volatile amines used to control pH of the feedwater and

prevent acid corrosion. Filming amines are typically long-chain cationic surfactants that reduce corrosion of metal surfaces in aqueous systems by forming a protective layer.[4]

Filming amines contain a hydrophilic and a hydrophobic end. The hydrophilic end of filming amine adheres to the metal surface, and the hydrophobic end makes the surfaces unwettable by creating a physical barrier against water, oxygen or other corrosive agents.[5] Figure 5.1 shows how filming amines act to protect metal surface against corrosion.

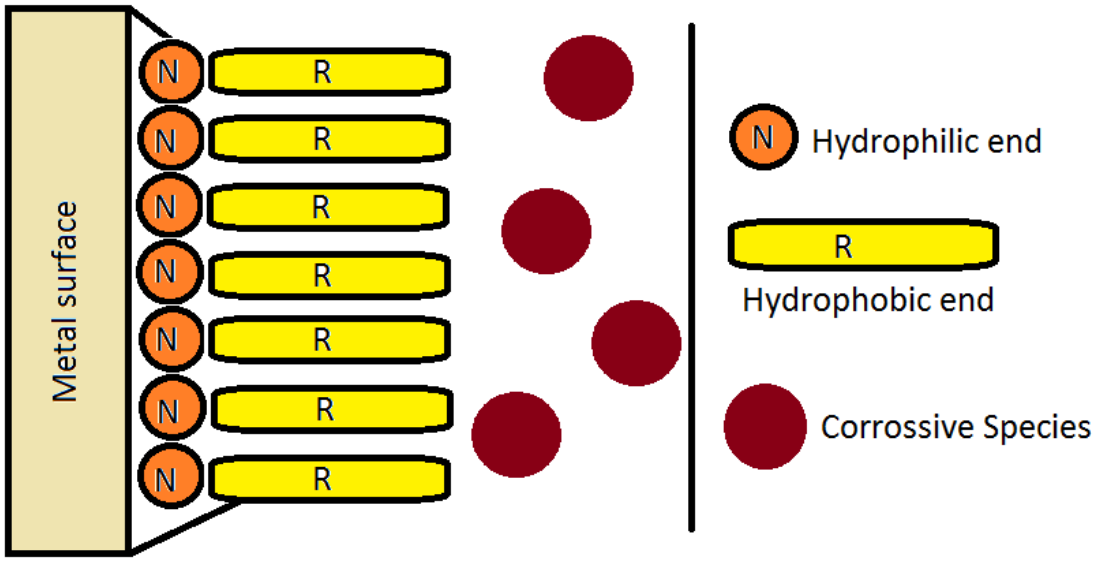

Figure 5.1: Role of filming amine to protect metal surface

Alkalizing and filming amines can foul ion exchange resins in different ways such as: physical surface blockage, permanent filling of space within the beads, establishment of surface charge to repulse diffusing ions, and permanent bonding with ion exchange sites that reduces effective exchange capacity. Raught et al. hypothesized that cation exchange resin reacts with amine, cleave sulfonate fragment, which then deposits on the anion exchange resins permanently.[6]

Little work had been done in the past on interaction between amines and ion exchange resins. Gönder et al. discussed fouling of anion exchange resins by organic acids such as humic and fluvic acid. The interaction of resins with ethanolamine, an alkalizing amine was also studied. The results showed, capacity losses were connected to both physical and chemical interactions.[7] This study is focused on providing evidences of amine adsorption by ion exchange resins.

Experimental: Uptake Capacity Measurement

Ion exchange resin uptake capacity is the total amount of a substance adsorbed in the resin matrix exposed to a concentrated solution. It can be expressed as moles per liter or kilograms of resin.

Materials:

DOWEX 650C cation exchange resin obtained from DOW chemicals, and Cyclohexylamine obtained from Aldrich were used for the experiment. For analysis, previously developed LCMS method was followed. HPLC grade acetonitrile was purchased from BDH VWR analytical, and deionized water collected at 18 megaohms were used as mobile phase. Trifluoroacetic acid purchased from Kodak was used to acidify the mobile phases.

Method:

Different amounts (10 to 500 mg) of standard H^+ form DOWEX 650C resins were exposed to a high concentration ($5x10^{-2}$ M) of cyclohexylamine solutions. The reaction mixtures were kept overnight (stirred occasionally) to ensure that the equilibriums were reached. Aliquots from each reaction mixture were separated and diluted adding deionized water to a range of the calibration curve. The samples were analyzed using LCMS and equilibrium concentrations were calculated. Cyclohexylamine uptake by DOWEX 650C was calculated from initial concentration, equilibrium concentration, and amount of resin.

Cyclohexylamine uptake was calculated using the following equation:

$$\text{Cyclohexylamine Uptake} = \frac{(C_0 - C_e)V}{M} \ (mol/kg)$$

C_0 = Initial cyclohexylamine concentration, C_e = Equilibrium cyclohexylamine concentration

V = Volume of cyclohexylamine solution, M = Mass of resin in kg

Result: Capacity Curve

The capacity curve was generated by plotting amine uptakes vs equilibrium concentrations. The amine uptake capacity was calculated from the maximum uptake of amines by ion exchange resins.

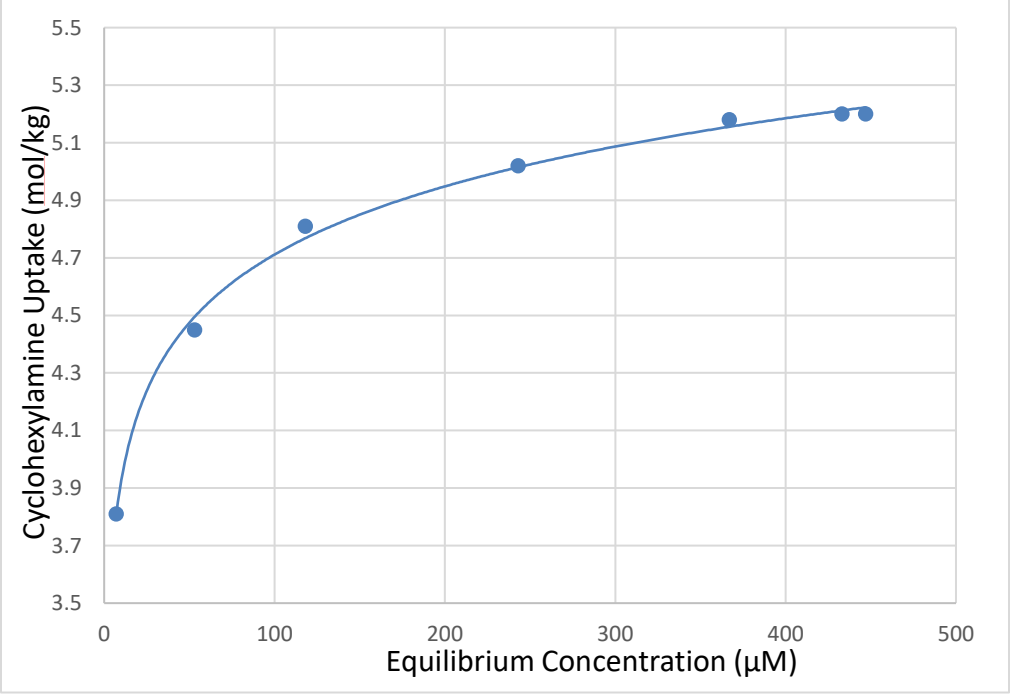

Figure 5.2: Capacity curve of cyclohexylamine uptake by DOWEX 650C at room temperature

The results were further evaluated with the Langmuir model ($q_e = \frac{Q_0 b C_e}{1+bC_e}$) to understand the nature of adsorption.[8] ($\frac{C_e}{q_e}$ vs C_e) was plotted and a straight line was obtained. Cyclohexylamine adsorption on DOWEX 650C perfectly followed the Langmuir adsorption model.

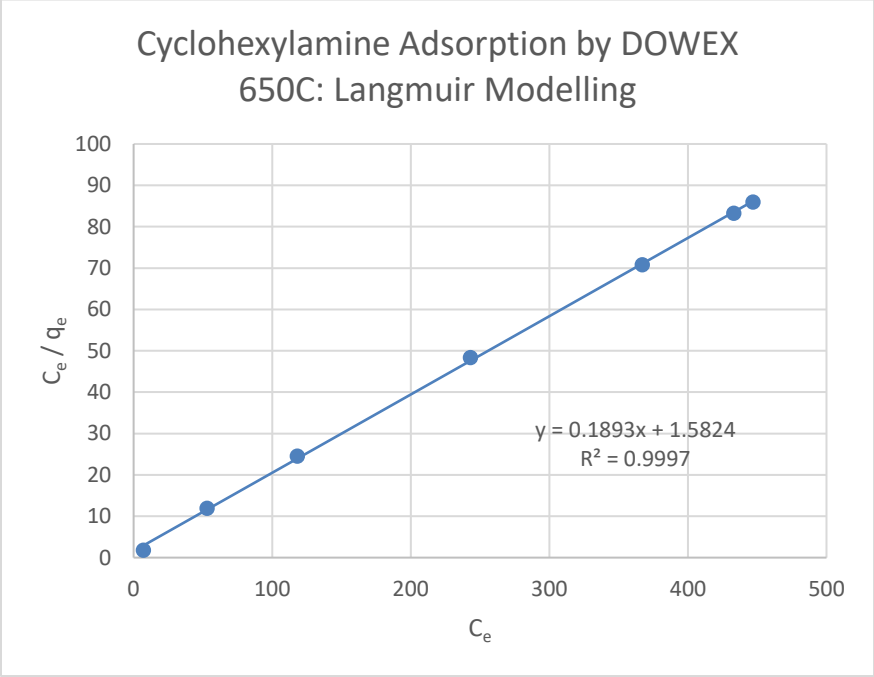

Figure 5.3: Langmuir adsorption modelling of cyclohexylamine adsorption by DOWEX 650C

q_e = amount of adsorbate in the adsorbent at equilibrium, b = Langmuir isotherm constant

Q_o = maximum monolayer coverage capacities, C_e = equilibrium concentration

Cyclohexylamine uptake capacity by DOWEX 650C was calculated as 5.3 mol/kg or 2.04 mol/L.

Experimental: Elemental Analysis

Elemental analysis is the process of analyzing the composition of elements in a sample. Since filming and alkalizing amines interact with ion exchange resins and the uptake capacity experiment showed that resins adsorb amines, a change in nitrogen to carbon ratio composition would support the results. DOWEX 650C cation exchange resin in standard (H^+), cyclohexylamine exposed, and regenerated forms were analyzed to compare the carbon nitrogen ratio.

Result and Discussion:

Resin Sample	Nitrogen %	Carbon %	Ratio (N : C)
Standard	0.04	33.35	0.001
Cyclohexylamine Exposed	4.00	58.33	0.069
Regenerated	0.95	43.18	0.022

Table 5.1: Nitrogen and carbon composition in different forms of DOWEX 650C resin

Standard form resins did not contain any significant amount of nitrogen. After exposing with cyclohexylamine, ratio of nitrogen to carbon increased to 0.069 that implied a significant amount of amine adsorption by the resins due to amine exposure. The regenerated DOWEX 650C had a nitrogen to carbon ratio of 0.022. The regeneration could not remove all the cyclohexylamine adsorbed.

Fluorescence Experiment:

Fluorescamine (4-phenylspiro(furan-2-(3H), 1' pthalan-3,3'-dione) is a non-fluorescing compound but it can react with primary amines to produce fluorophor.[9] The reaction is shown in Figure 5.4.

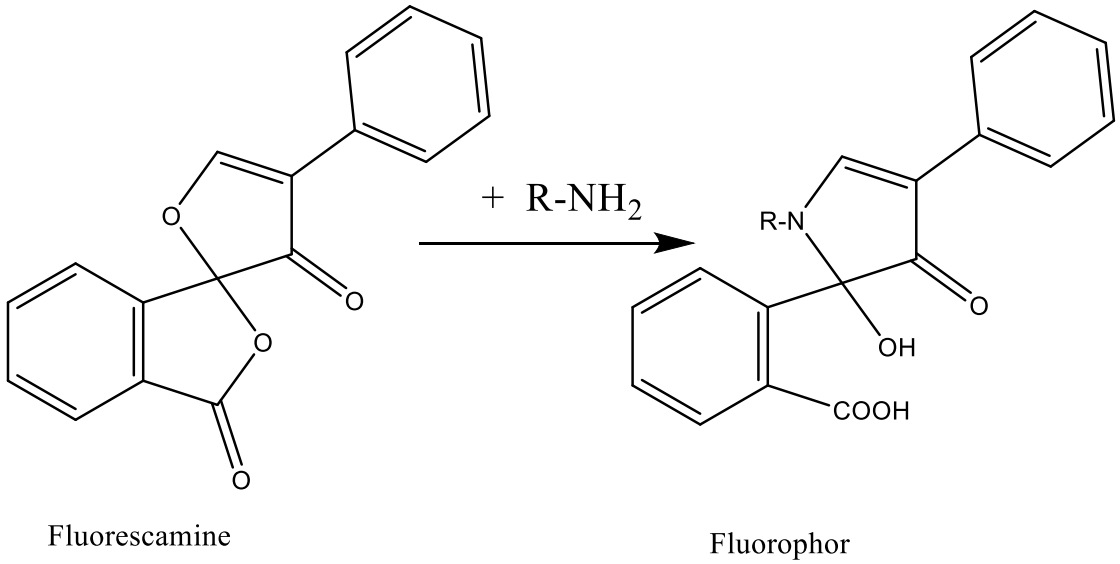

Figure 5.4: Reaction of fluorescamine with primary amines [9]

Strong base anion exchange resins contain quaternary ammonium groups that does not react with fluorescamine. After exposure, any adsorbed amine can react with fluorescamine and fluorescence will result.

Experimental:

Materials and Method:

DOWEX 550A in standard (OH^-), Cetamine (a commercial filming amine) exposed and regenerated forms were treated with fluorescamine to analyze fluorescent properties by ultra-violet (UV) excitation. A method developed by Bartos et. al was followed. [10] 0.02% Fluorescamine solution was prepared in acetone. By mixing 0.2 M boric acid and 0.2 M potassium chloride, a buffer solution was prepared with a pH of 8.5. Resin beads were placed on a petri dish and a few drops of buffer solution was added. After few seconds, few drops of fluorecsamine solution was added. The beads were allowed to air dry and taken to the dark room. A hand-held UV lamp was used to excite the fluorophor and pictures were taken using a digital camera. The Figure 5.5 shows the fluorescence response of DOWEX 550A in different forms.

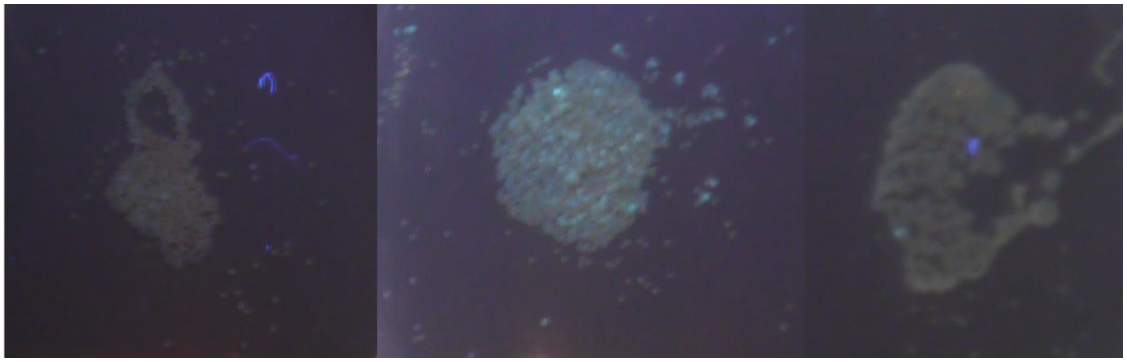

Figure 5.5: Fluorescence (short wave UV excitation, 254 nm) of DOWEX 550A resin: standard (left), exposed to Cetamine (middle), and regenerated (right)

Result and Discussion:

The results showed there was no fluorescence for standard OH^- form DOWEX 550A. Higher fluorescence was observed for Cetamine exposed resin, and lower intensity was found for regenerated DOWEX 550A after Cetamine exposure. As expected, quaternary ammonium functional groups in DOWEX 550A anion exchange resin remain fluorescence inactive after treating with fluorescamine. Fluorescence observed for Cetamine exposed resin provided the evidence of amine adsorption by anion exchange resin and it also showed that some of the amines are not removed after regeneration.

Conclusion:

All the experiments provided evidences of amine uptake by ion exchange resins. Uptake capacity measurement, elemental analysis and fluorometric experiment results showed that both cation and anion exchange resins adsorbed amines. Cation exchange resins are expected to uptake amines since they can form positively charged ionic species by taking up the protons from the resins and then attach to the functional groups.

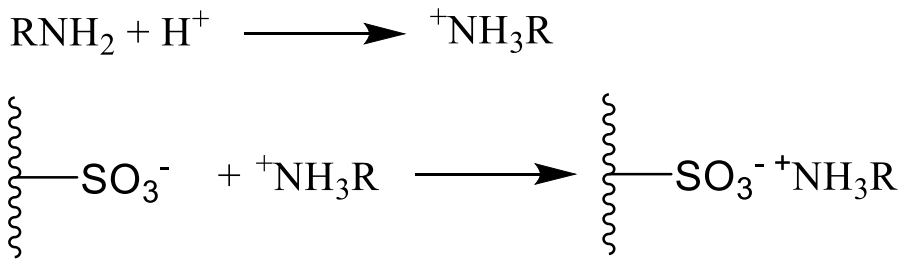

Figure 5.6: Attachment of amines by ion exchange in cation exchange resin

Adsorption in the anion exchange must followed binding to the polymeric backbone or resin surface. Most importantly, elemental analysis and fluorometric analysis showed that for both anion and cation exchange resins, regeneration could not remove all the amines adsorbed during the exposure.

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CHAPTER VI

SALT SPLITTING KINETICS OF AMINE EXPOSED ION EXCHANGE RESINS

Introduction:

Kinetic study of ion exchange resin is very important to design ion exchange column and determine the state of resin for practical application. The goal of kinetic study of standard, amine exposed, and regenerated resin is to understand the change in resin performance. Fouling of resin by different alkalizing and filming amines, described in the previous chapters, indicated a loss in the total exchange capacity. Both exposed and regenerated, cation exchange and anion exchange resins suffered exchange capacity loss.[1]

Mass transfer coefficient (MTC) is one way to understand the effect of fouling on resin performance. MTC is the rate at which ions move from the solution to the ion exchange site. A low MTC indicates that the rate of ion exchange is slower compared to the flow of water containing contaminant ions.[2] The concentration of contaminant ion in the feedwater after leaving the resin bed is known as kinetic leakage. The flow rate of water is set in a way that ensures that the resin column reaches close to its exchange capacity and saturates with ions without showing kinetic leakage. At this condition, the entire resin bed in the column acts as exchange zone.

With the increase of degree of fouling, ion exchange resins exhibit higher resistance to ionic mass transfer. Kinetic leakage will occur faster at the same flow rate, or at the same time for a slower flow rate for fouled resin. Ion leakage will start before the all the exchangeable sites in the resin bed are occupied. A reduction in MTC will be observed.[3]

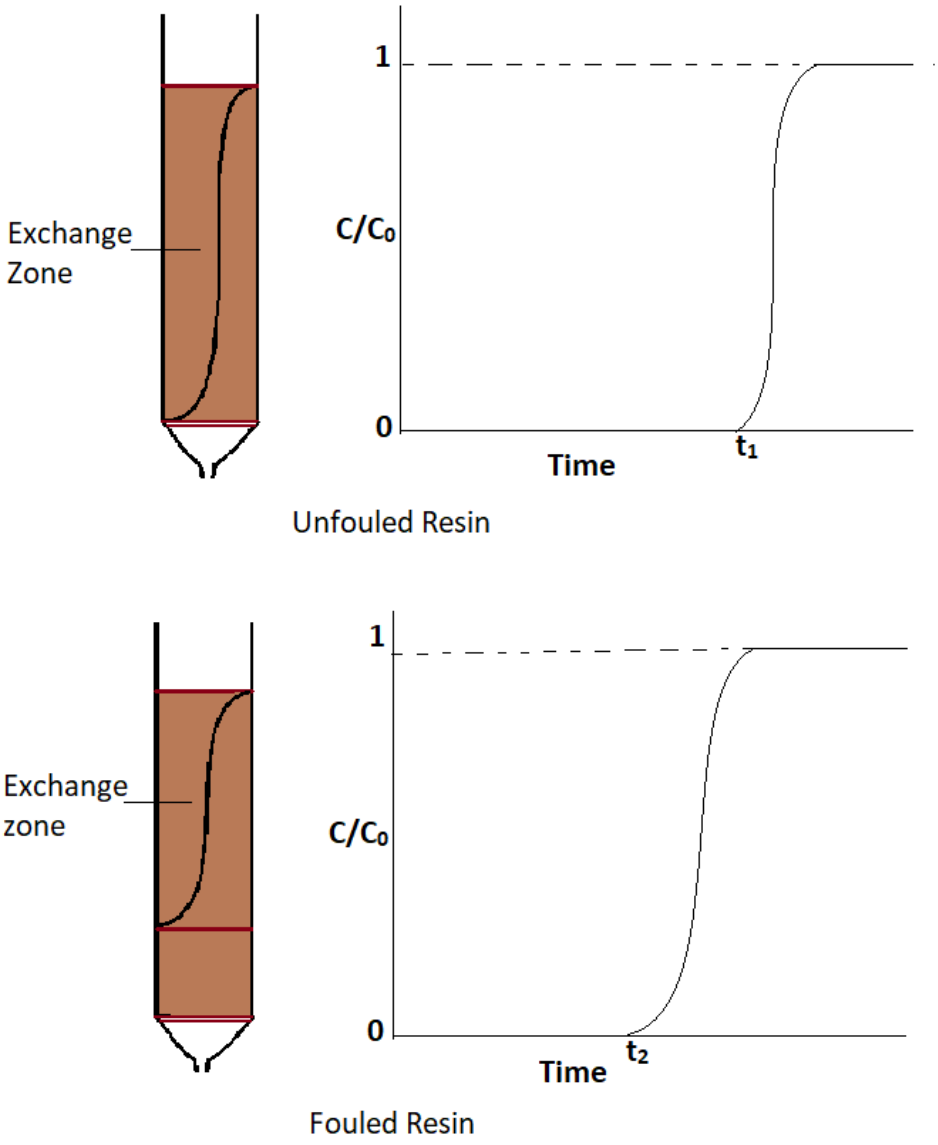

Figure 6.1: Exchange zone and breakthrough curve for unfouled and fouled resin

The rate of ion exchange in ion exchange resin can be calculated by measuring the rate of change in acidity.[4] HCl and NaOH can be produced when NaCl reacts with cation exchange resin in H^+ form, and anion exchange resin in OH^- form respectively.

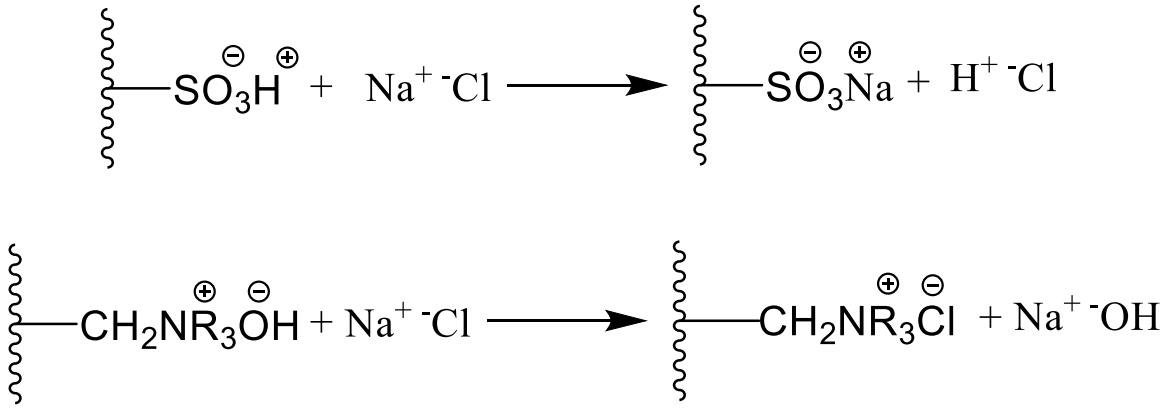

Figure 6.2: Salt splitting by cation (top) and anion (below) exchange resin

Salt splitting capacity of an ion exchange resin is the measure of the number of sites acting as strong acid or base. For strong acid cation exchange resin and strong base anion exchange resin, salt splitting capacity is the major component of the total resin exchange capacity.[5] Salt splitting kinetic studies are important to understand how the resins will perform as condensate polishers. The results provide actual rate of ion exchange by the resins.

Experimental:

Materials and method:

DOWEX 650C cation exchange resin (DOW Chemicals), DOWEX 550A anion exchange resin (DOW Chemicals), cyclohehylamine (Aldrich), octylamine (Acros Organics), Cetamine (commercial filming amine), sodium chloride (Fisher Scientific), pH 7 buffer.

Resins in standard, amine exposed, and regenerated forms were used to compare the rate of ion exchange and influence of fouling by amines on salt splitting rates. A pH meter coupled with Vernier LabQuest system was used for automated data collection. The pH meter was calibrated at pH 7 using a buffer. 40 mL of 0.2 M NaCl solution measured and transferred to a 50-mL beaker, the beaker was placed on the magnetic stirrer platform. The pH meter was washed with deionized water and put into the beaker. 1 g cation exchange resin was weighed and added to the beaker containing NaCl solution, the software was started simultaneously to collect pH vs time data. NaCl solution was used in excess so that the reaction rate was independent of NaCl concentration. The rates were found to be faster for anion exchange resins, to follow the kinetics, 0.5 mL anion exchange resin was reacted with 40 mL 0.1 M NaCl.

Figure 6.3: Set up for salt splitting kinetic experiments

Results and Discussion:

The reactions followed zero order kinetics, the initial rates were fast and that was used for rate calculation. The following graph (Figure 6.4) shows the kinetic data of cyclohexylamine exposed and regenerated resin with respect to standard DOWEX 650C.

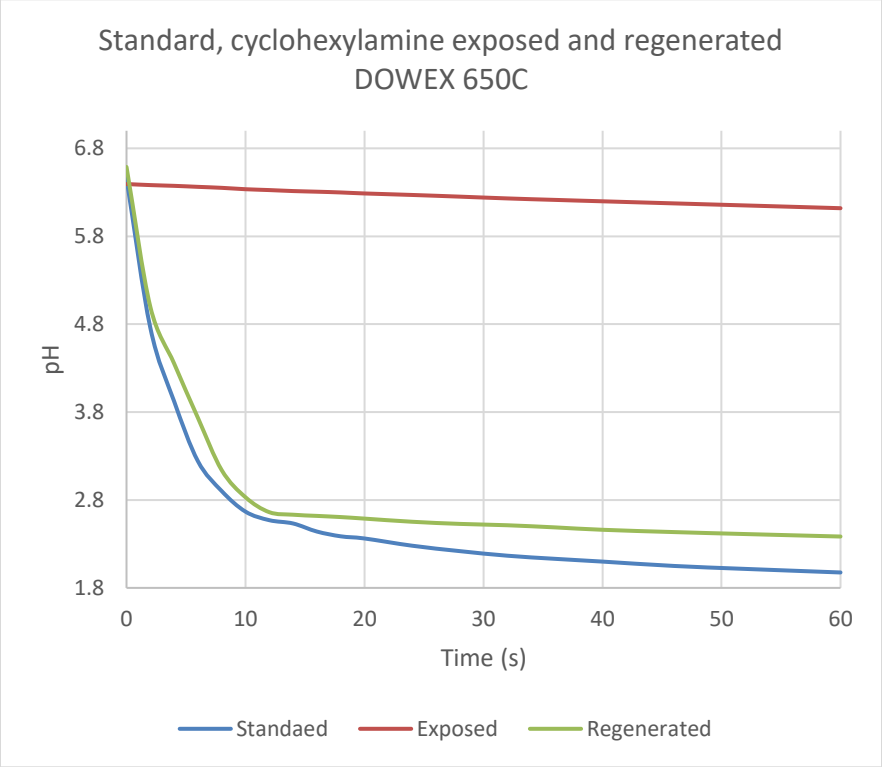

Figure 6.4: pH vs time: standard, cyclohexylamine exposed, and regenerated DOWEX 650C

Cyclohexylamine exposed DOWEX 650C did not change pH significantly after addition of NaCl. The rate was (6×10^{-9} M/s) found to be very slow compared to the rate for standard resin (3×10^{-4} M/s). The regenerated DOWEX 650C after exposing with cyclohexylamine showed a rate of 2×10^{-4} M/s, that was 33% slower than the standard resin.

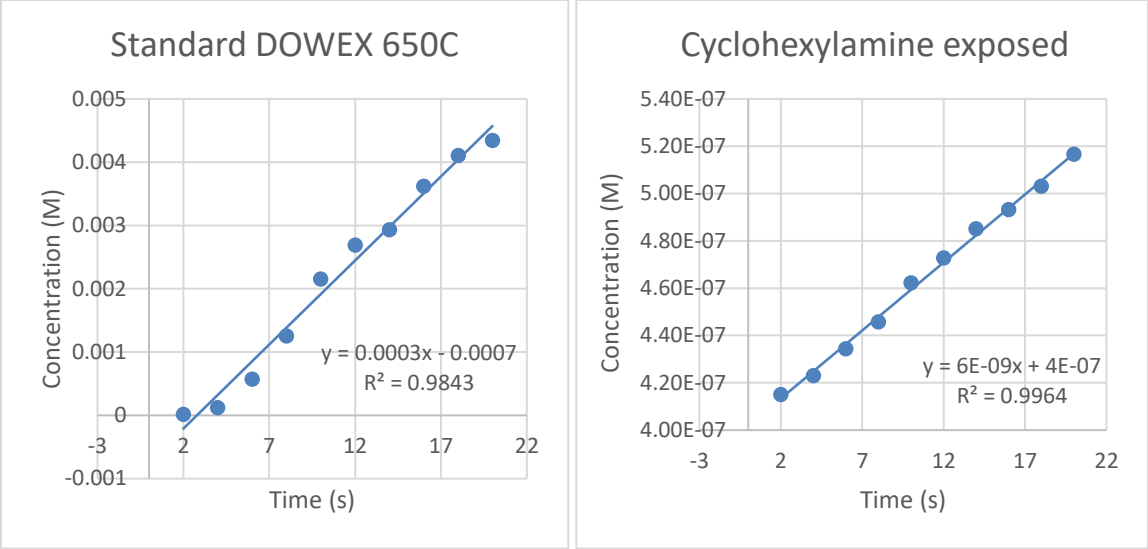

Figure 6.5: Initial rate comparison: standard (left), and cyclohexylamine exposed (right) DOWEX 650C cation exchange resin.

The reaction rate results were consistant with the exchange capacity loss results found in the Chapter IV. Cyclohexylamine, an alkalizing amine, completely occupied all the exchangable sites in DOWEX 650C cation exchange resin, and the exchange capacity was found to be 0. The pH change was also found to be negligible after NaCl addition which showed that there were barely any H^+ present in the cyclohexylamine exposed DOWEX 650C. After regeneration, a 26% exchange capacity was unrecovered, that also influenced the rate, salt splitting rate for regenerated resin was 33% slower than that of standard resin. The final approaching pH in Figure 6.4 also suggested that the regenerated resin had less H^+ available compared to standard DOWEX 650C.

Octylamine, a filming amine, also affect the salt splitting kinetics in a similar fashion. Figure 6.6 shows the kinetic data that compares change of pH with time after NaCl addition to standard, octylamine exposed, and regenerated DOWEX 650C cation exchange resin.

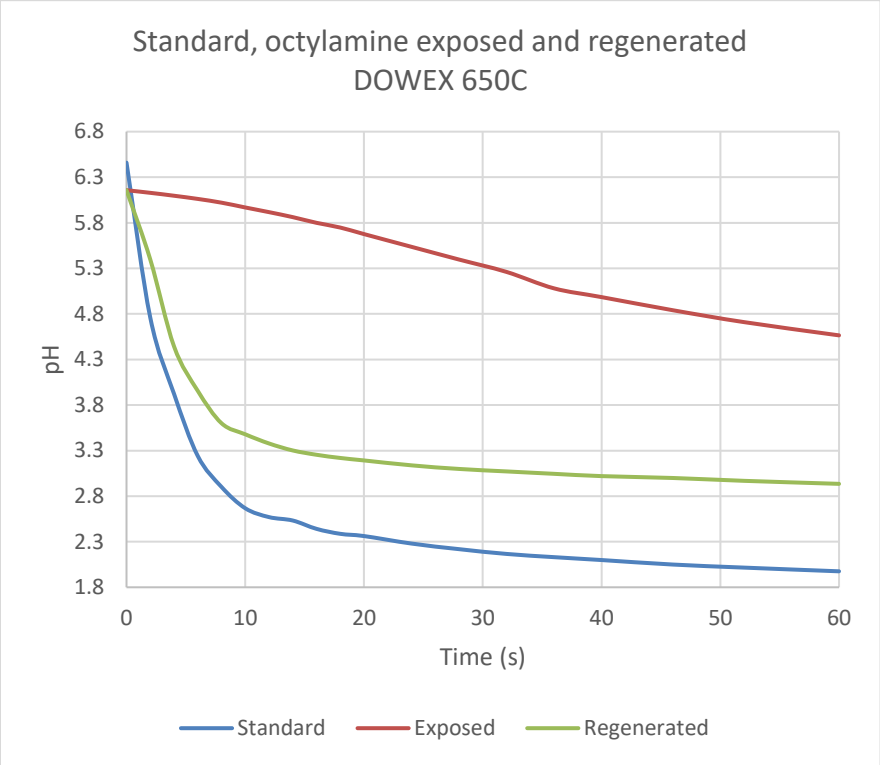

Figure 6.6: pH vs time: standard, octylamine exposed, and regenerated DOWEX 650C

The initial rates for exposed and regenerated resins were calculated as 7×10^{-8} M/s, and 4×10^{-5} M/s respectively. With respect to standard resin, the rate of salt splitting was very slow for octylamine exposed DOWEX 650C cation exchange resin. After regeneration, the rate was still 7.5 times slower.

A commercial amine, Cetamine reduced the salt splitting rate to 5 x 10^{-5} M/s, that was 6 times slower than standard form DOWEX 650C (3 x 10^{-4} M/s). After regeneration, the rate was close to the salt splitting rate for standard resin, but the projected final pH showed that less number of H^+ were available in the regenerated form compared to the standard form resin.

The pH vs time data is shown in Figure 6.7.

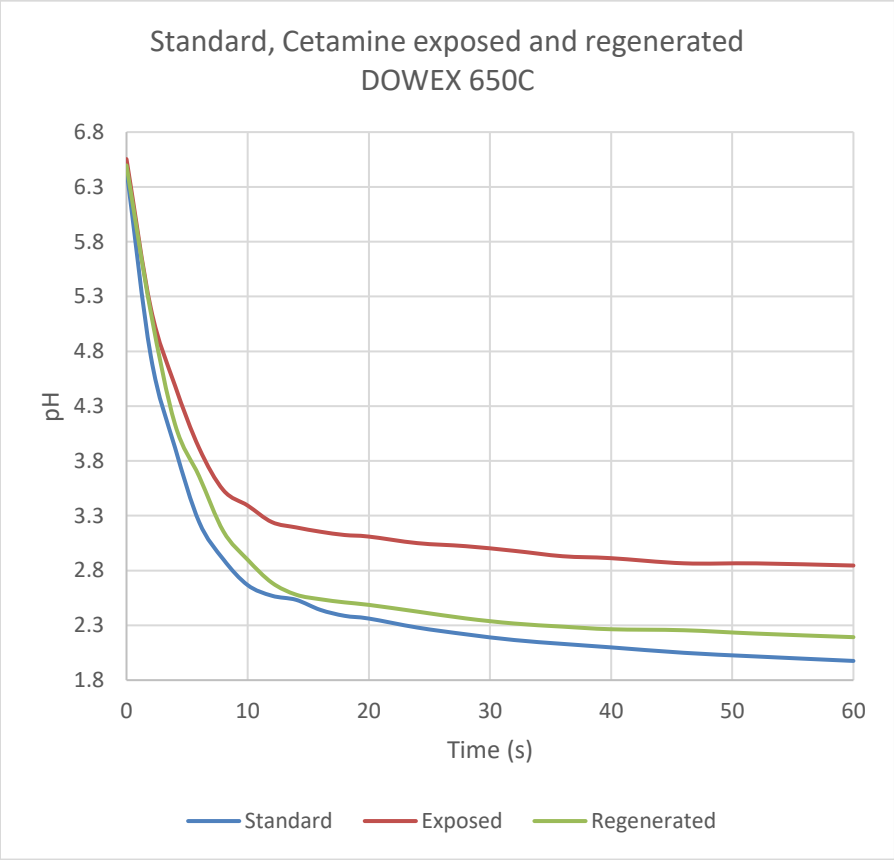

Figure 6.7: pH vs time: standard, Cetamine exposed, and regenerated DOWEX 650C

All three amines significantly affected the ion exchange kinetics of DOWEX 650C cation exchange resin after exposure, regeneration failed to recover the original rate and exchange capacity.

Anion exchange resin salt splitting kinetics were also affected by the use of cyclohexylamine, octylamine, and Cetamine. The following graph (Figure 6.8) shows the change in pH vs time data for standard, cyclohexylamine exposed, and regenerated DOWEX 550A.

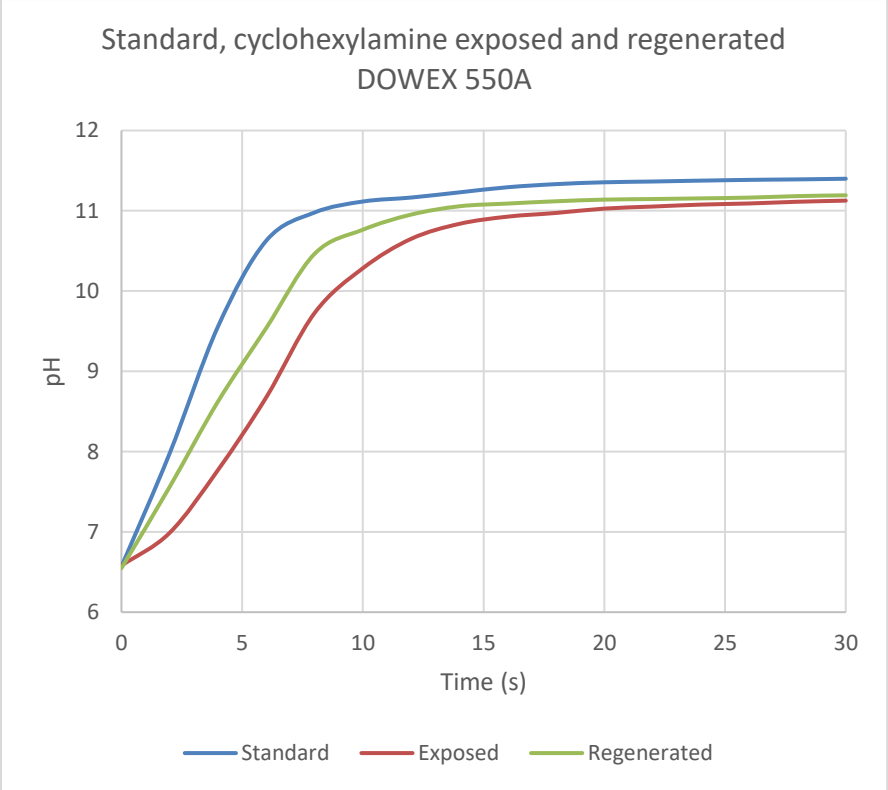

Figure 6.8: pH vs time: standard, cyclohexylamine exposed, and regenerated DOWEX 550A

The initial rate of salt splitting for standard DOWEX 550A was 1 x 10^{-4} M/s, 20% decrease in rate (0.8 x 10^{-4} M/s) was found for cyclohexylamine exposed resin. The regenerated resin also showed similar rate as standard resin. Cyclohexylamine reduced DOWEX 550A resin exchange capacity only by 4% (Chapter IV), this may also have resulted in a slight decrease in the salt splitting kinetics. After regeneration, the projected pH in Figure 6.8 shows a decrease in exchangeable OH^- concentration.

Octylamine affects the salt splitting rate much more than cyclohexylamine. The rate decreased to 3 x 10^{-6} M/s for octylamine exposed resin from 1 x 10^{-4} M/s (standard). After regeneration the rate was found to be 5 x 10^{-5} M/s, that was 20 times slower than the salt splitting rate of standard DOWEX 550A anion exchange resin. Figure 6.9 shows the pH vs time data for standard, octylamine exposed, and regenerated DOWEX 550A.

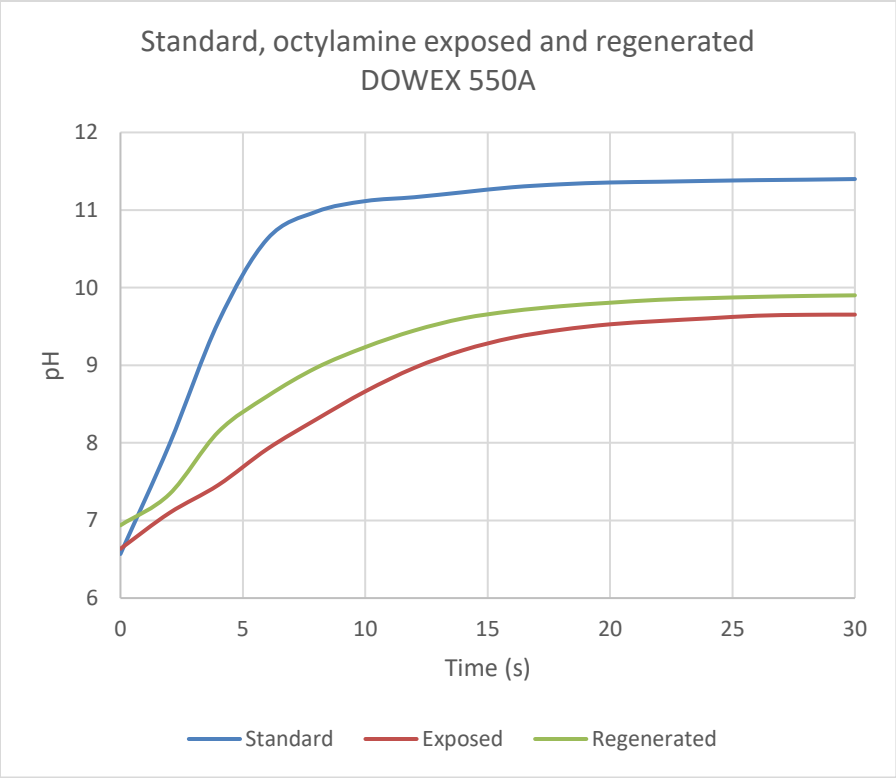

Figure 6.9: pH vs time: standard, octylamine exposed, and regenerated DOWEX 550A

As found in Chapter IV, octylamine exposure caused 29% loss in the exchange capacity of DOWEX 550A, after regeneration, the exchange capacity was 18% less than standard resin. The hydrophobicity of octylamine, a filming amine may have played a role on the salt splitting kinetics of the resin.

Conclusion:

Both cation (DOWEX 650C) and anion (DOWEX 550A) exchange resin salt splitting kinetics was affected by the exposure of alkalizing (cyclohexylamine) and filming amines (octylamine and Cetamine). Octylamine had much greater impact compared to cyclohexylamine amine due to larger size and hydrophobicity. The results were also consistent with the exchange capacity loss results. Such decrease in salt splitting rate can cause significant problems in the applied fields by lowering the mass transfer coefficient (MTC) and breakthrough time. Part of this research was collaborated with the Department of Chemical Engineering at Oklahoma State University. The results showed a 18-25% MTC loss of DOWEX 650C by the exposure of filming amines.

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CHAPTER VII

SYNTHESIS OF NANOMETRIC AGGREGATES OF MOLYBDANUM (VI) AND THUNGSTANE (VI) OXIDE FROM ANION EXCHANGE RESIN

Introduction

Recent development of nanotechnology and use of nanomaterials have grown into a wide range of applications. Figure 7.1 shows different fields of application of nanotechnology.[1] Nanoparticles show significant difference in their chemical properties and reactivity as compared to their bulk counterparts due to their smaller size, higher surface area, unusual crystal shapes, and lattice orders.[2] Metal oxide nanoparticles have received special attention since they have applications in various areas such as medicine,[3] metal coating,[4] dye degradation,[5] cosmetic additive, and catalytic materials.[6-7]

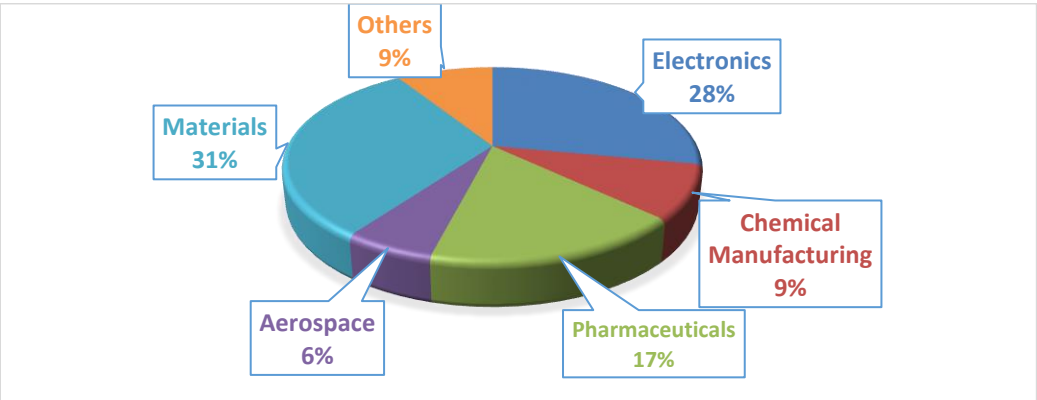

Figure 7.1: Applications of nanotechnology [1]

Pollution remediation and water treatment are among novel applications of such materials.[8-9] Nanoparticles provide more surface area, that led to higher adsorption of the contaminant species. Method of synthesis of nanoparticles has a significant effect on their properties. Ceramic method,[10] hydrothermal and solvothermal methods,[11] and sol-gel methods [12] are widely used. In practical applications, the apparent advantage of small size can cause clogging of filter due to facile suspension of the particles, and high operating pressure is required. Porous spherical aggregates on nanoparticular metal oxides are suitable for overcoming such drawback without losing too much chemical reactivity. Due to their shape, they can be packed in columns to increase interaction with flowing systems. These materials would also be suitable for applications in the field of catalysis.

Spherical aggregates of nanoparticulate iron, zinc, nickel, and aluminum oxides were previously prepared by the Apblett's group using cation exchange resins. These materials were used for arsenic, uranium remediation, dye removal from water.[13-14] Molybdenum trioxide, MoO_3, have been used in number of important applications such as electrochromism,[15] photochromism,[16] and catalysis.[17] Tungsten trioxide is used in photochromic, electrochromic,[18] and thermochromic devices, also for gas sensing applications.[19] The synthesis of nanometric aggregates of molybdenum (VI) and tungsten (VI) oxide using anion exchange resin will be discussed in this chapter.

Synthesis of spherical aggregate of MoO_3

Materials and Method:

Standard (OH^-) form DOWEX 550A, a strong base anion exchange resin, purchased from Aldrich in the form of spherical beads was used. $Na_2MoO_4 \cdot 2H_2O$ obtained from Alfa Aesar was used as molybdenum source. To incorporate molybdenum to the resin beads, 200 mL 0.5 M solution of sodium molybdate was passed through a column containing 25 mL of resin at a flow rate of 1 ml/min. A higher concentration and 5 equivalent moles of MoO_4^{2-} was used so that all the exchangeable groups can be replaced, each MoO_4^{2-} could replace 2 OH^- groups to maintain charge neutrality. The resins in the column was washed by adding deionized water and the conductivity of the eluent was checked until it went to zero. The resins were then collected and air dried for further experiments and treatments.

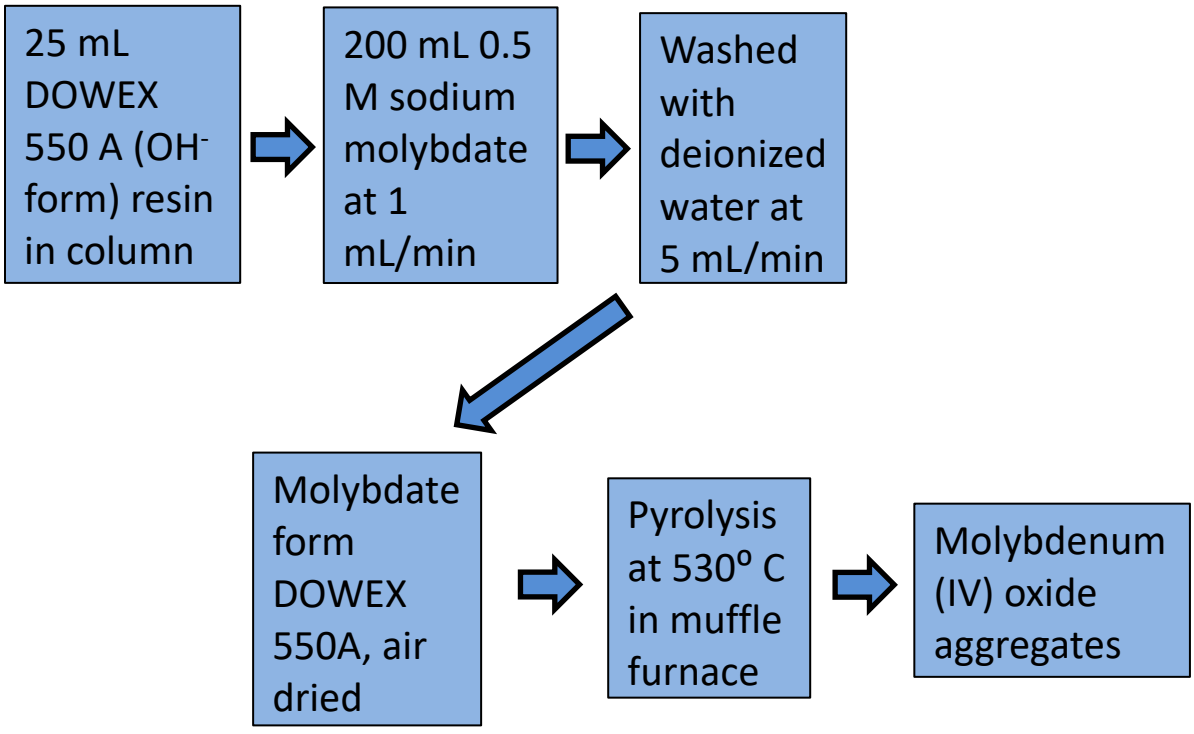

Figure 7.2: Preparation of molybdenum (IV) oxide aggregates

Thermogravimetric analysis (TGA) was first performed to find out the temperature required to convert the molybdate form resin to spherical molybdenum oxides. Using the results from TGA, the molybdate form resin beads were pyrolyzed at 530 ºC using a ramp of 4 ºC for 12 hours to get the final product. The material was characterized using BET method for surface area analysis, and scanning electron microscopy (SEM) was performed to understand the morphology.

Thermogravimetric Analysis (TGA):

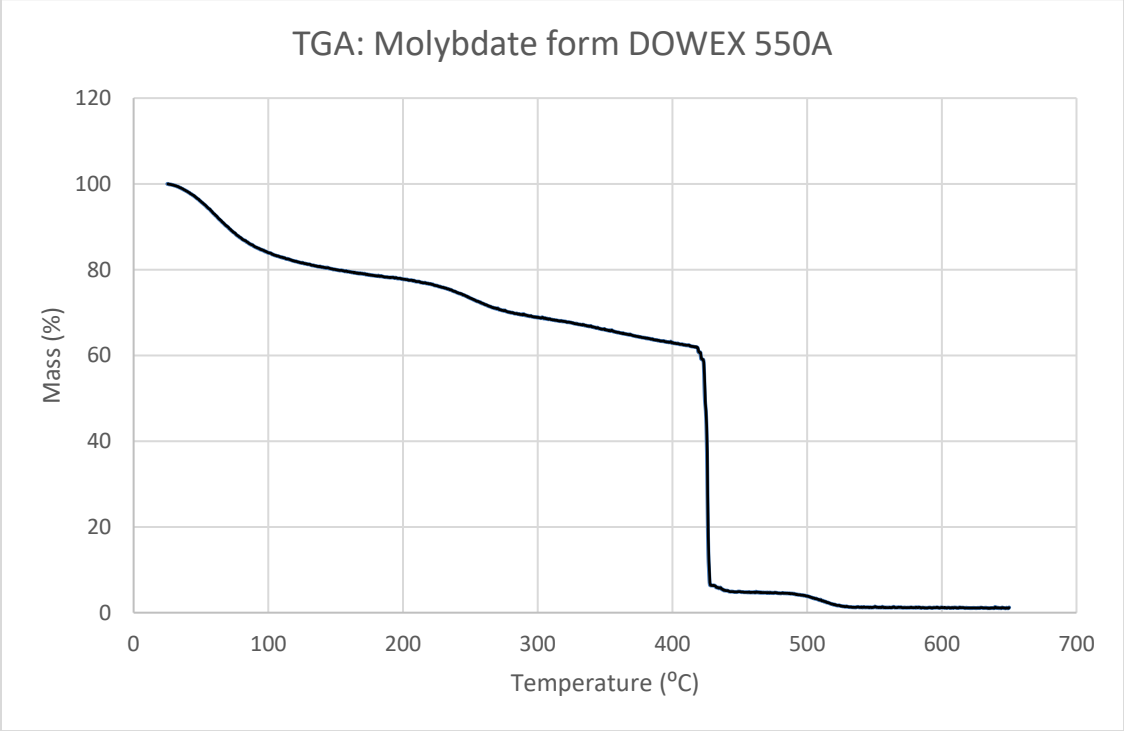

Figure 7.3: Thermogravimetric analysis (TGA) trace for molybdate loaded DOWEX 550A resin

The thermogravimetric experiment was performed using approximately 12 mg of sample on a Seiko ExStar 6500 TGA/DTA instrument under a 50 mL/min flow of dry air. The temperature was ramped from 25 ºC to 700 ºC at a rate of 5 ºC/min. the material lost approximately 20% by

weight of water between room temperature and 150 ºC. Above this temperature gradual decomposition of the ion exchange resin occurred up to 415 ºC and a sharp decrease in mass was found. A final mass loss was observed between 495 ºC to 520 ºC and formation of molybdenum oxide was complete.

Scanning Electron Microscopy (SEM):

Scanning electron microscope (SEM) images were taken using a JEOL JXM 6400 SEM at Oklahoma State University Microscopy Lab.

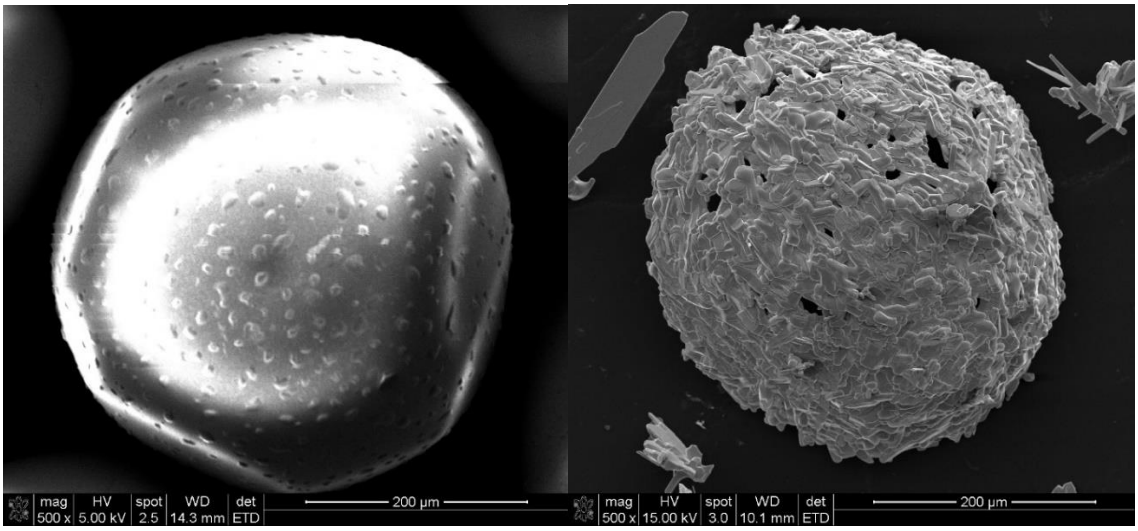

Figure 7.4: Scanning electron microscopy images of molybdenum loaded resin before (left) and after (right) pyrolysis at 530 ºC

The images showed that most of the resin beads were broken during pyrolysis, few spherical particles with a diameter of 250 – 300 µm were found. Porous aggregates of smaller particles

were observed, broken spheres showed formation of crystalline particles of different sizes and shapes. The inner part of the spheres contained smaller particles compared to the particles formed on the outer part. At higher magnifications, the particles were found to be formed as nanolayers of molybdenum (IV) oxide.

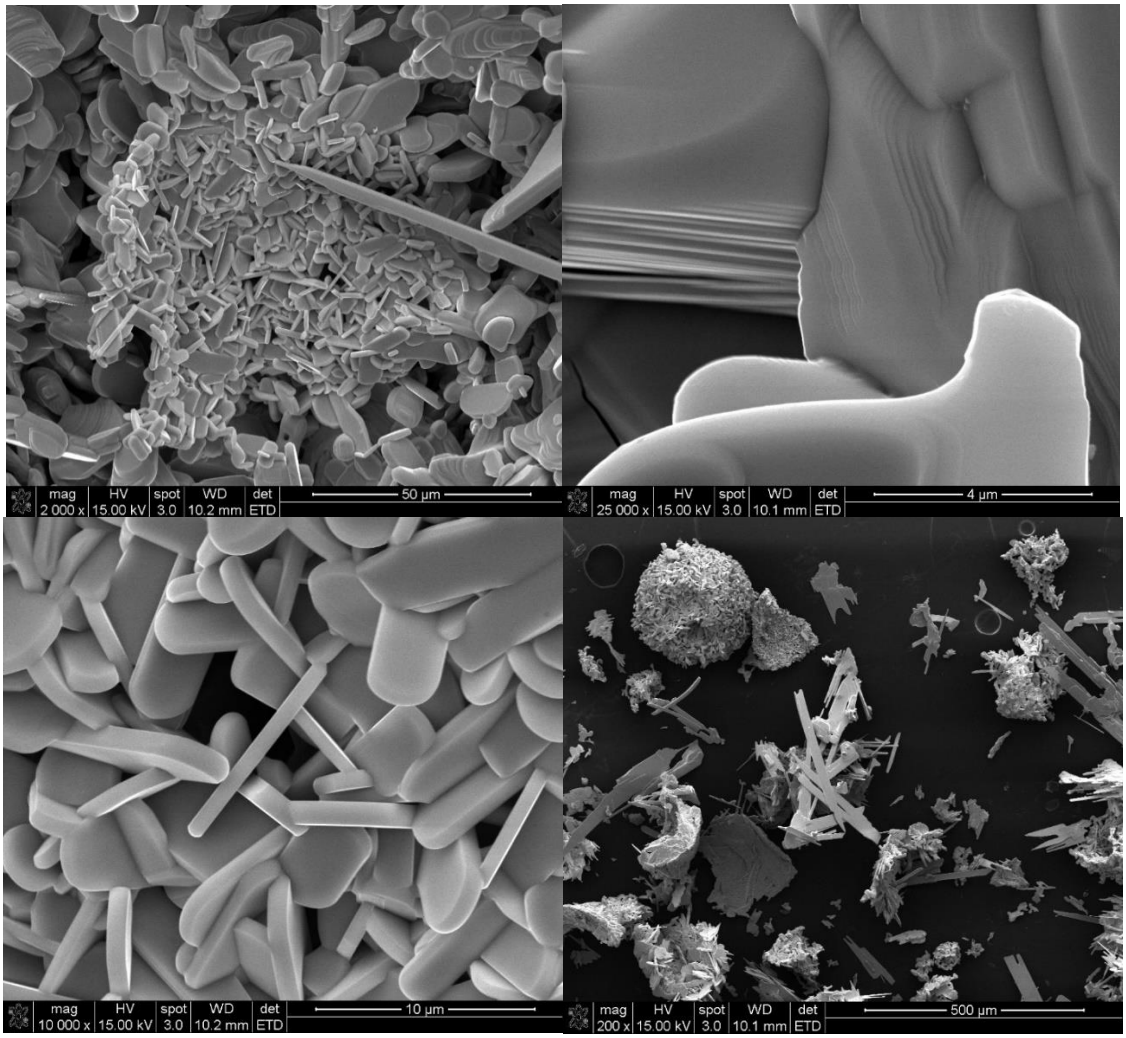

Figure 7.5: Scanning electron microscope images of molybdenum (IV) oxide aggregates

Surface Area:

Surface area analysis of the material was measured by nitrogen adsorption isotherm on a Quantachrome Nova 10 instrument using the Brunauer, Emmett, and Teller analysis method. The specific surface area of molybdenum (VI) oxide was found to be 61.6 m^2/g.

Synthesis of Spherical Aggregate of WoO_3

Materials and Method:

The synthesis of nanometric tungstic oxide was carried out similarly as of molybdenum oxide. Standard (OH^-) form DOWEX 550A, a strong base anion exchange resin was treated with $Na_2WO_4 \cdot 2H_2O$ (Alfa Aesar). 200 mL 0.5 M solution of sodium tungstate was added to a column containing 25 mL of resin, a flow rate of 1 ml/min was maintained.

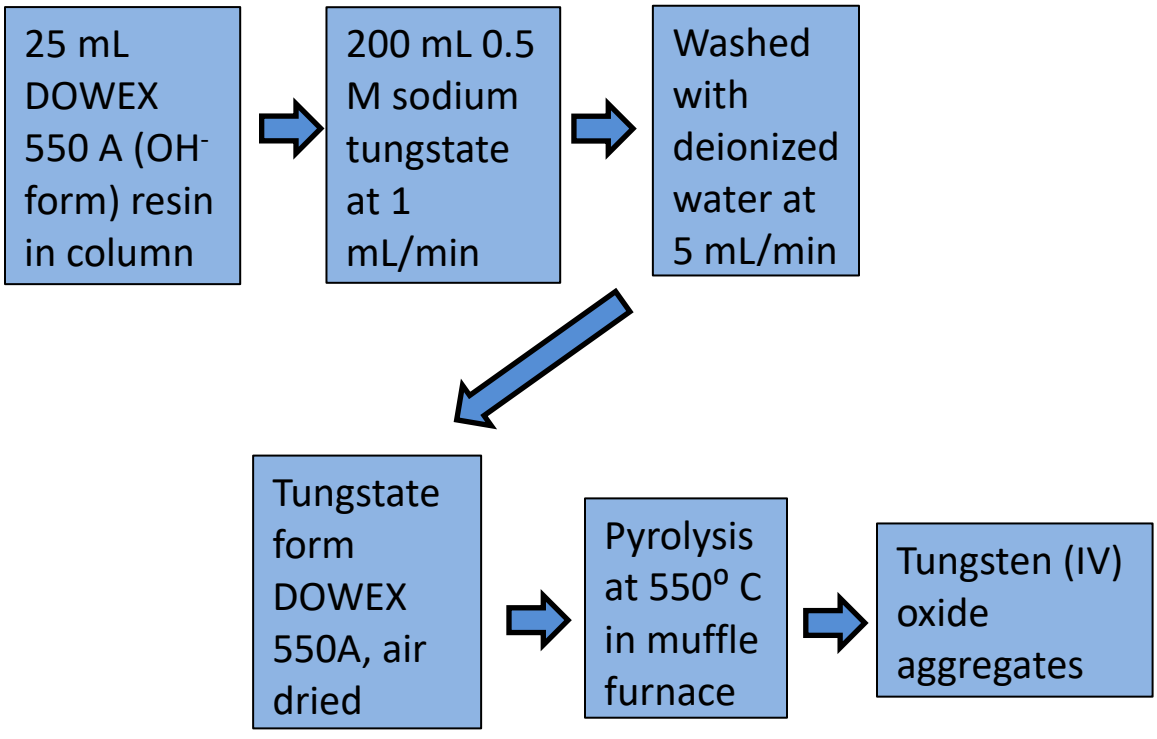

Figure 7.6: Preparation of tungsten (VI) oxide aggregates

To ensure complete exchange, a higher concentration and 5 equivalent moles of WO_4^{2-} was used, each WO_4^{2-} could replace 2 OH^- groups to maintain charge neutrality. After conversion of resin to tungstate form, the column was washed by adding deionized water and the conductivity of the eluent was checked until it went to zero. The resins were then collected and air dried for further experiments and treatments.

Thermogravimetric analysis (TGA) was performed, from TGA result, the pyrolysis temperature was set as 550 ºC. Tungstate form resin beads were pyrolyzed at 550 ºC using a ramp of 4 ºC for 12 hours to get the final product. The material was characterized using BET method for surface area analysis, and scanning electron microscopy (SEM) was performed to understand the morphology.

Thermogravimetric Analysis (TGA):

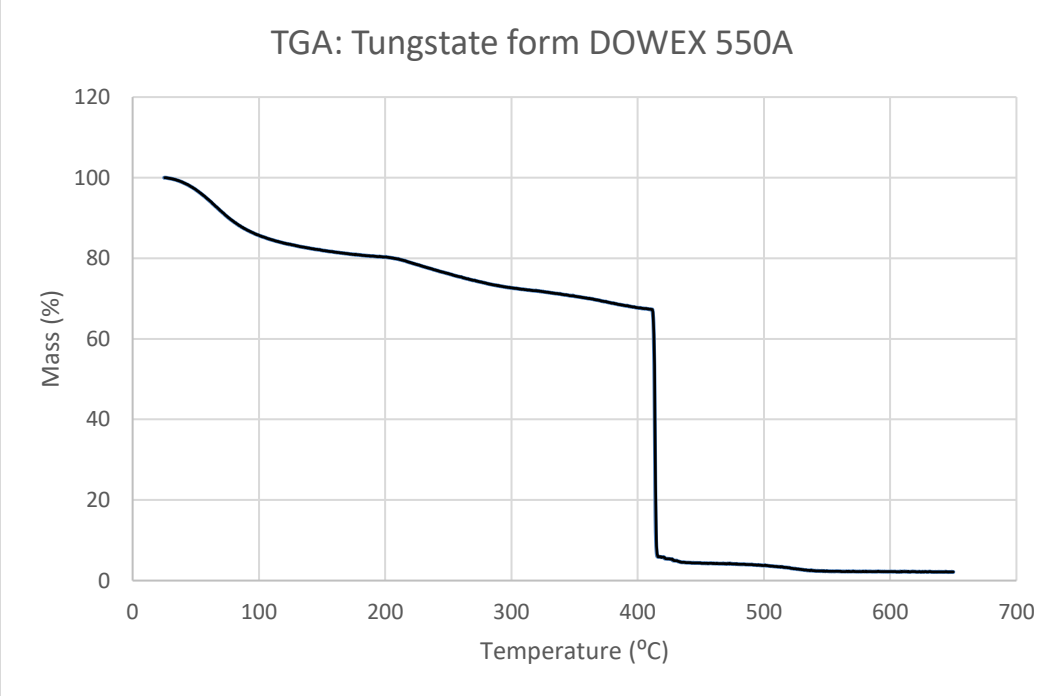

Figure 7.7: Thermogravimetric analysis (TGA) trace for tungstate loaded DOWEX 550A resin

The thermogravimetric experiment was performed using approximately 12 mg of sample on a Seiko ExStar 6500 TGA/DTA instrument under a 50 mL/min flow of dry air. The temperature was ramped from 25 ºC to 700 ºC at a rate of 5 ºC/min. the material lost approximately 18% by weight of water between room temperature and 150 ºC. Above this temperature gradual decomposition of the ion exchange resin occurred up to 415 ºC and a sharp decrease in mass was found. A final mass loss was observed between 495 ºC to 530 ºC and formation of tungsten (IV) oxide was complete.

Scanning Electron Microscopy (SEM):

Scanning electron microscope (SEM) images were taken using a JEOL JXM 6400 SEM at Oklahoma State University Microscopy Lab.

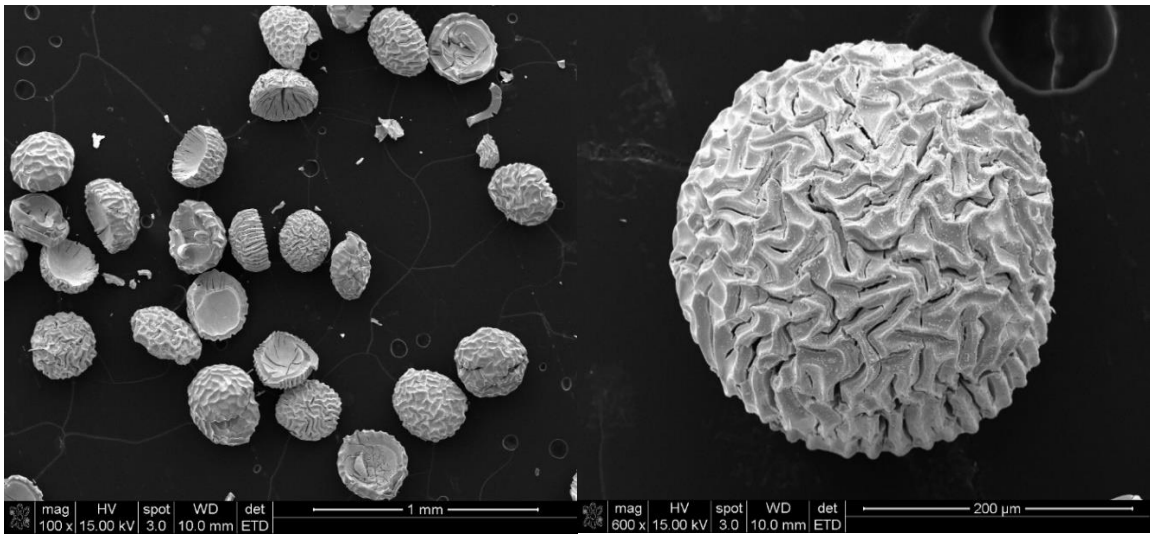

Figure 7.8: Scanning electron microscopy images of tungsten loaded resin after pyrolysis at 550 ºC

The images showed a different result for tungsten (IV) oxide prepared by pyrolysis of tungstate form DOWEX 550A resin. The spherical shape of the resin beads was preserved mostly as half spheres. Unbroken spherical particles had a diameter of 250 – 300 µm. The spheres / half spheres consisted of condensed WO_3 throughout, they were composed of aggregates of nanoparticles those fused together to form larger particles. The particles could be easily crushed into fine powder using a mortar and pestle, but they did not break easily into smaller particles by shaking in a glass vial. The material was highly porous, many channels and pores were created during the pyrolysis process.

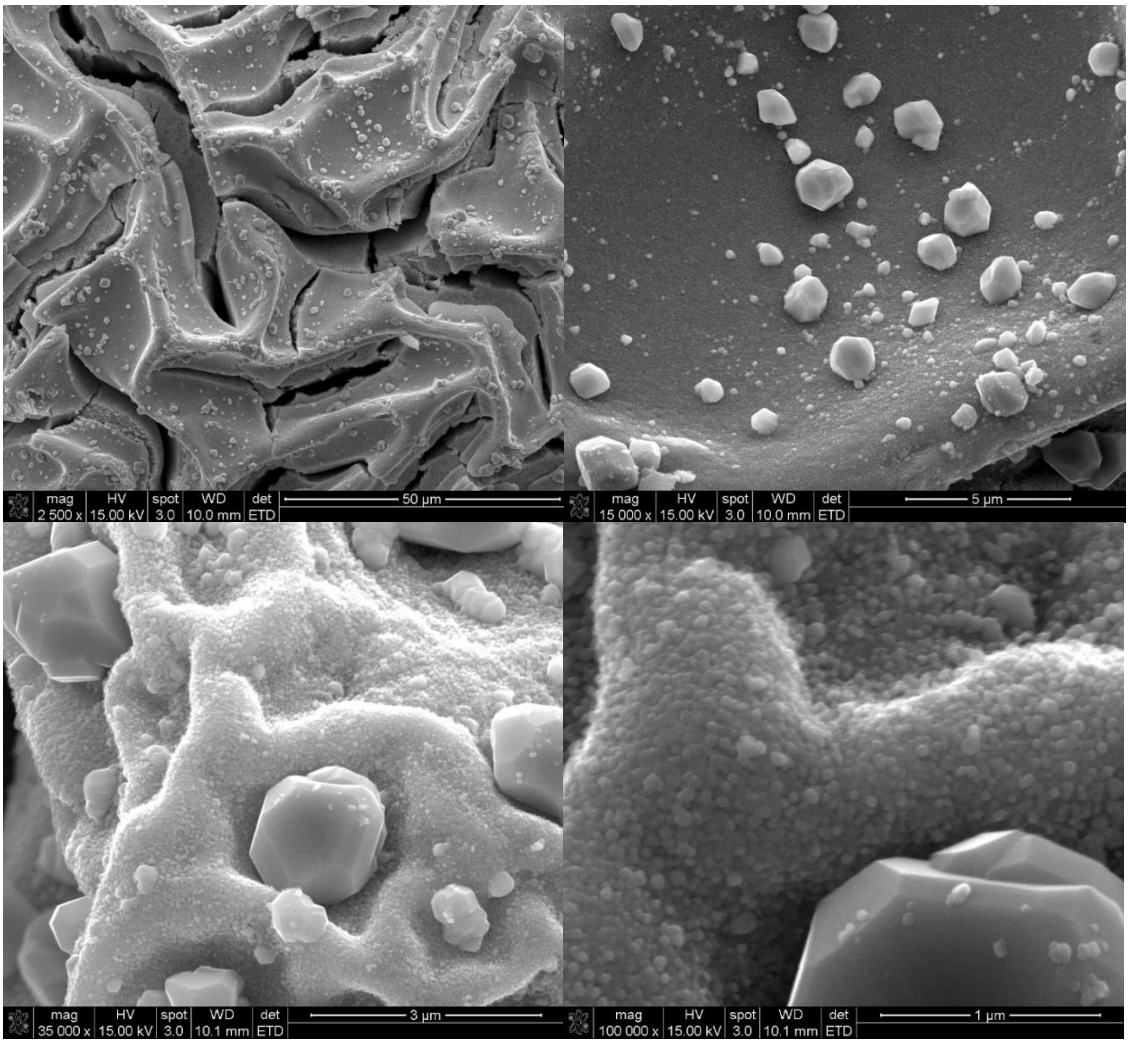

Figure 7.9: Scanning electron microscope images of tungsten (IV) oxide nanoparticle aggregates

Surface Area:

Surface area analysis of the material was measured by nitrogen adsorption isotherm on a Quantachrome Nova 10 instrument using the Brunauer, Emmett, and Teller analysis method. The specific surface area of tungsten (VI) oxide was found to be 41.1 m^2/g.

Conclusion

Pyrolysis of tungsten loaded DOWEX 550A anion exchange resin at 550 ºC yielded half spheres of WO_3. Molybdenum loaded DOWEX 550A pyrolyzed at 530 ºC produced broken fragments, the resin shape was not preserved. Water, carbon dioxide, and nitrogen dioxide were the main byproducts of pyrolysis. The surface area for molybdenum (IV) oxide was 61.6 m^2/g, and for tungsten (IV) oxide the surface area was measured as 41.1 m^2/g. X-ray diffraction (XRD) experiments will be performed to determine crystallinity and crystallite size. The SEM images shows thin nanometric layer formation during molybdenum (IV) oxide formation. Tungsten (IV) oxide SEM images at higher magnification shows agglomeration of nanoparticles. Future study by changing parameters such as resin type, crosslinking, degree of functionalization, temperature, etc. will help to have more control over shape and particle size. The advantage of controlled shape and surface area will make such aggregates of nanomaterials useful for catalytic, environmental remediation, and biomedical applications.

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CHAPTER VIII

CONCLUSION AND FUTURE WORK

Alkalizing and filming amines are used as corrosion inhibitors in condensate systems, but they can be responsible for copper alloy corrosion at higher concentrations. They can also end up in the polishing ion exchange resin chamber to foul resin. Amines are hard to analyze due to their basic character. In this study a simple and direct injection method for analyzing amines using liquid chromatography mass spectrometry (LCMS) was developed. The method works for both alkalizing and filming amines, also for mixture of amines, industrial formulation usually contains a mixture of an alkalizing and a filming amine. A 10 μM limit of detection was achieved, the method perfectly suits for the concentration range of industrial application of alkalizing and filming amines. The newly developed LCMS method does not require any pretreatment of the samples, use of expensive reagents, or buffer solutions, and analysis of amines can be done at a quick time.

Effect of ion exchange resin properties by the use of alkalizing and filming amines was studied extensively. The effect on ion exchange capacity of cation and anion exchange resins were studied using 10 different alkalizing, filming, and commercial amines. Alkalizing amines completely occupied exchangeable sites of cation exchange resins, after regeneration, 20-30% exchange capacity was un recovered. For anion exchange resin, a 4-8% loss of exchange capacity was observed for both amine exposed and regenerated resins. Since alkalizing amines are small in

size, and water soluble, the loss in exchange capacity of resins after regeneration may resulted in due to some chemical reaction with the functional groups or resin backbone. Future investigations are required to understand the mechanism how alkalizing amines occupy, block, or react with the resin to reduce exchange capacity.

Filming amines also had greater effect on cation exchange resins compared to anion exchange resins. Anion exchange resin exchange capacity loss was much more when they were exposed to filming amines. The chain length and hydrophobicity played an important role in the exchange capacity loss. Linear, long hydrophobic tail containing filming amines only occupied exchangeable sites near surfaces, regeneration was very poor for such amines. Shorter and nonlinear chain amines lowered the exchange capacity more after exposure, regeneration was also better.

Besides exchange capacity, other resin properties such as apparent density and moisture content were also affected by the use of these amines. hydrophobic filming amines significantly affected the moisture contents of different resins. Failure of polishing resins due to amine exposure has economic effect, and also risk of power plant accidents. Future research is required to understand how these amines act on resin, and find possible ways to overcome such problem.

The ion exchange kinetic behaviors of resins were also affected by amine exposure. For both cation and anion exchange resins, slower salt splitting rates were observed for amine exposed resins compared to standard resins. The rates improved after regeneration but were found to be slower than standard resins.

An approach was made to prepare spherical aggregates of transition metal oxide nanoparticles from metal loaded ion exchange resins. Anion exchange resins loaded with molybdate were pyrolyzed at 530 ºC to prepare aggregates of molybdenum (IV) oxide that had a surface area of 61.6 m^2/g. Semi spherical, porous aggregates of tungsten (IV) oxide were prepared by firing

tungstate form anion exchange resins at 550 ºC. These materials can be used for medical, environmental, and catalytic uses.

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